Solar Thermochemical Fuel Production – Overview on the work carried out by the German Aerospace Center DLR

Sandia National Laboratories, Albuquerque, NM
June 25th 2015

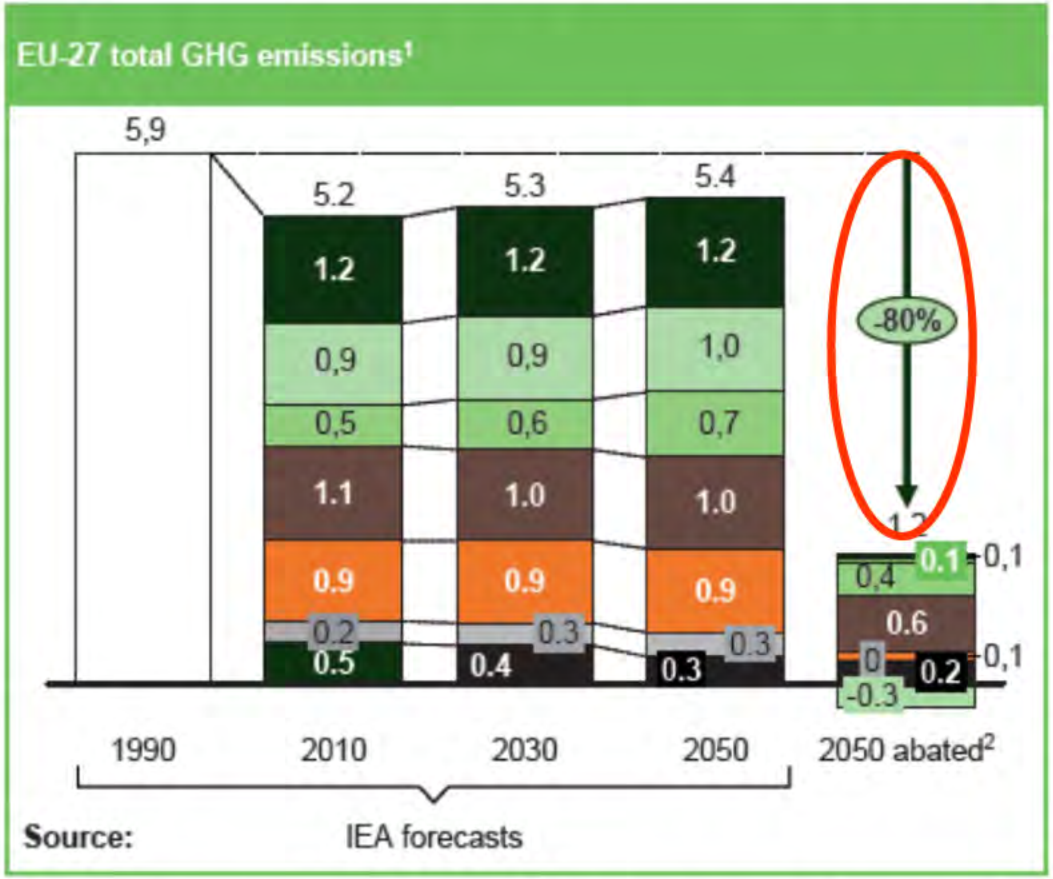
Dr. Christian Sattler
Christian.sattler@dlr.de

DLR

Political Drivers: Examples – EU Sustainable Energy Technology Plan (SET-Plan 2007) G7 Goals (2015)

- **Goals of the EU until 2020 (20/20/20)**
  - **20%** higher energy efficiency
  - **20%** less GHG emission
  - **20%** renewable energy
- **Goal of the EU until 2050:**
  - **80%** less CO_2 emissions than in 1990
- **G7 Goals, Elmau, Germany**
  - **100%** Decarbonisation until 2100
  - **100 bln $/year** for climate actions in developing countries, large share by industrial investment

Development of EU GHG emissions [Gt CO_2e]



Sector	Total abatement
Power	95-100%
Road transport	95%
Air & sea transport	50%
Industry[3]	40%
Buildings	95%
Waste	100%
Agriculture	20%
Forestry	-0.25 Gt CO_2e

1 Large efficiency improvements are already included in the baseline based on the International Energy Agency, World Energy Outlook 2009, especially for industry

2 Abatement estimates within sector based on Global GHG Cost Curve

3 CCS applied to 50% of large industry (cement, chemistry, iron and steel, petroleum and gas, not applied to other industries)

SOURCE: www.roadmap2050.eu

DLR

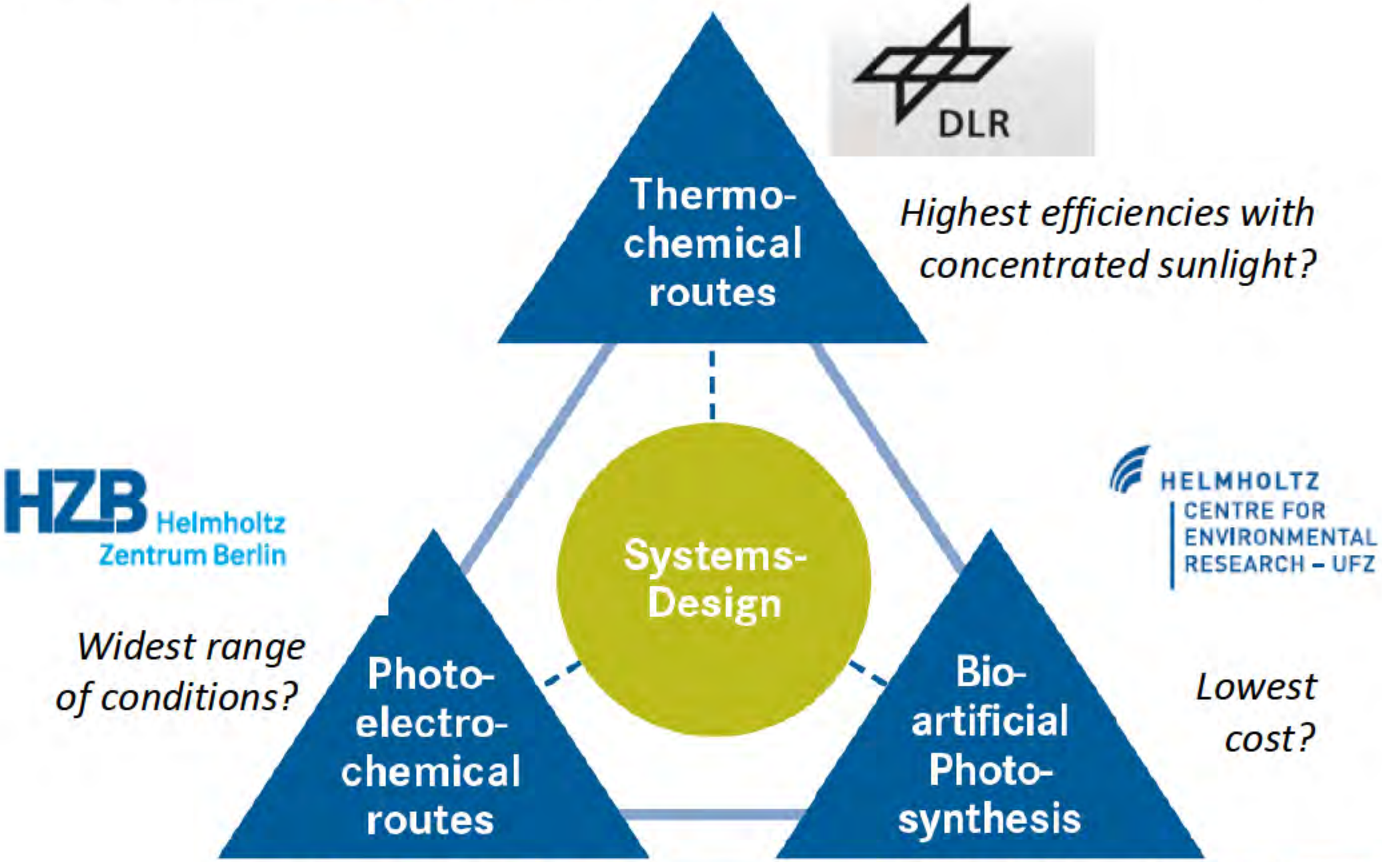
Programs in Europe

- **National Energy Research Programs** in most of the European Countries (very different levels and aims)
- **German Solar Fuels Program** was evaluated as outstanding this year and will be the fastest growing topic on renewable energy in large scale research over the next five years
- Joint Programs under the **European Framework Programmes** for Research and Technical Development (RFP)
- 2014 – 2020 **„HORIZON 2020“** - Wider focus than the previous seven RFPs: It combines all **research and innovation funding** provided through the RFP, the innovation related activities of the Competitiveness and Innovation Framework Programme (CIP) and the European Institute of Innovation and Technology (EIT)
- **Participation of partners from outside the European Research area**

German Strategy and Approach on Solar Fuels

Goal in the Helmholtz Association

To demonstrate stand-alone, viable systems for the emission-free production of chemical fuels – especially **Hydrogen** - with sunlight



DLR

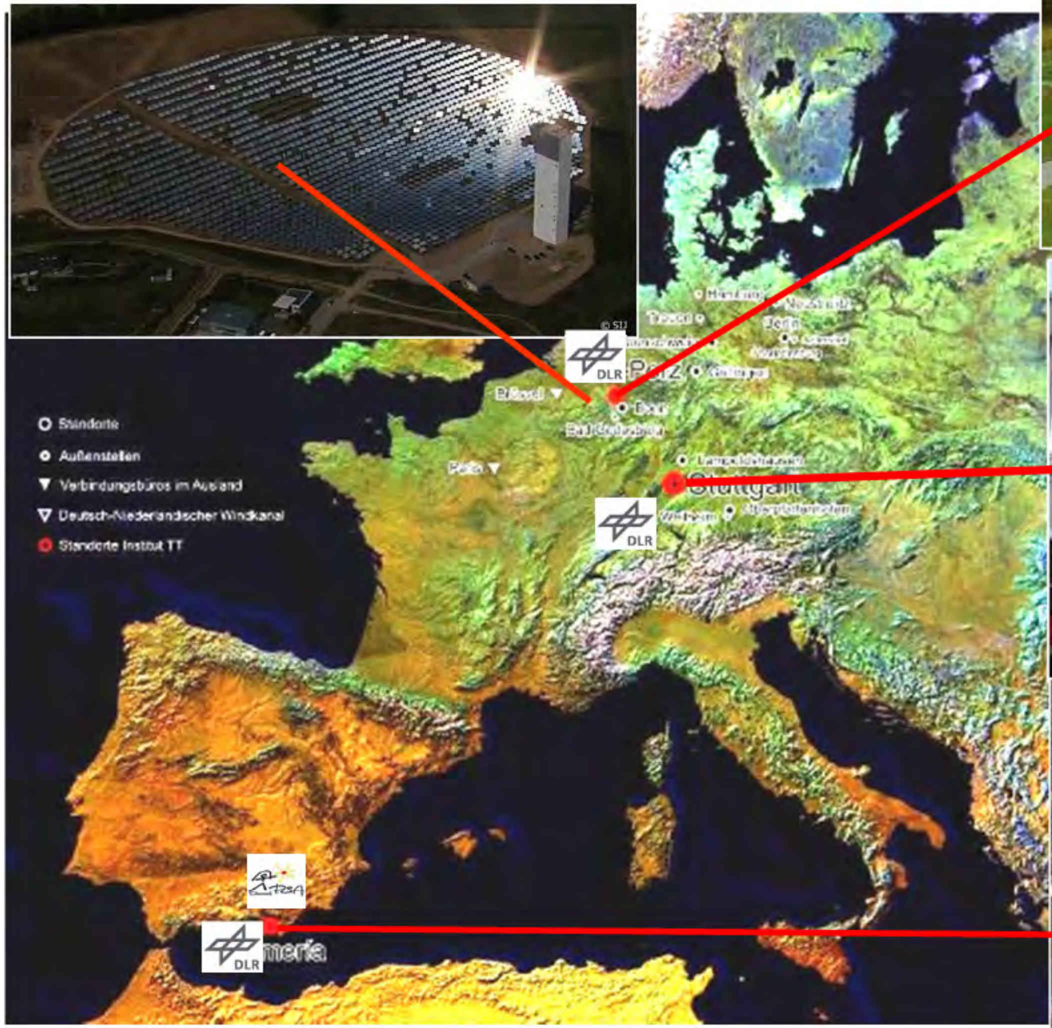
DLR German Aerospace Center

- Research Institution
- Space Agency
- Project Management Agency

>8000 employees across
32 institutes and facilities at
■ 16 sites.

Offices in Brussels, Paris,
Tokyo and Washington, Almería.

DLR Institute of Solar Research



160 staff, 20 M€/a, 4 sites

Institute of Solar Research

Directors

Prof. Dr. Robert Pitz-Paal/ Prof. Dr. Bernhard Hoffschmidt

Point-Focus Systems
Dr. Reiner Buck (34 P)

Line-Focus Systems
K. Hennecke (16 P)

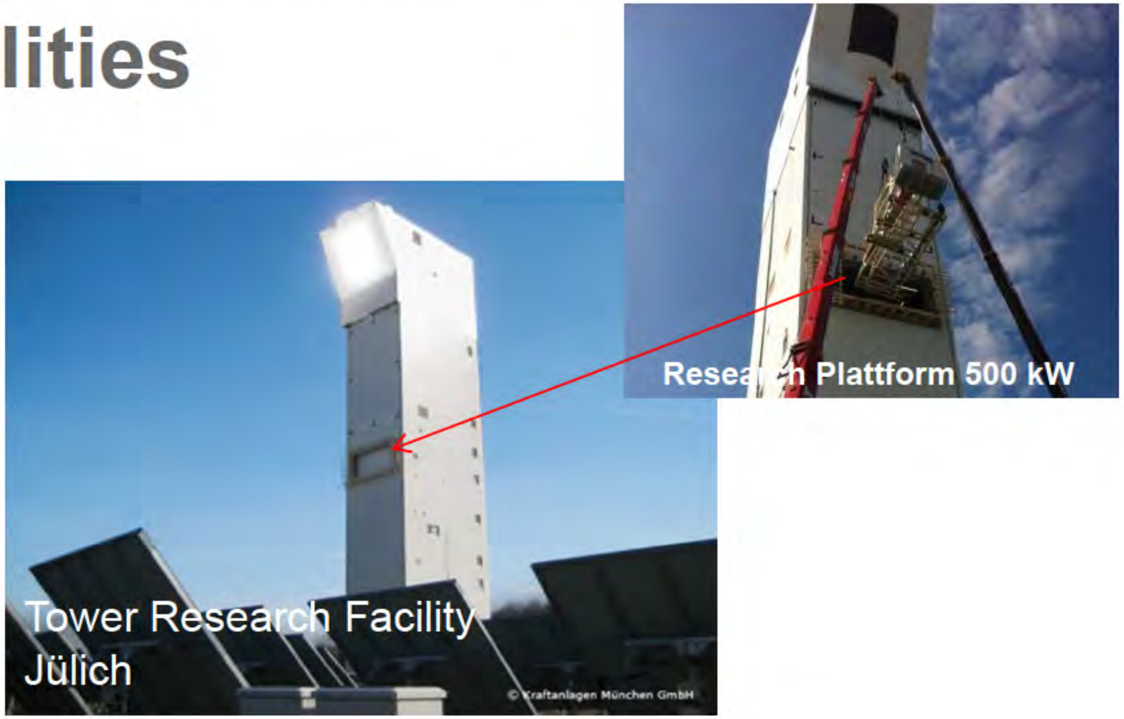
Qualification
Dr. P. Heller (33 P)

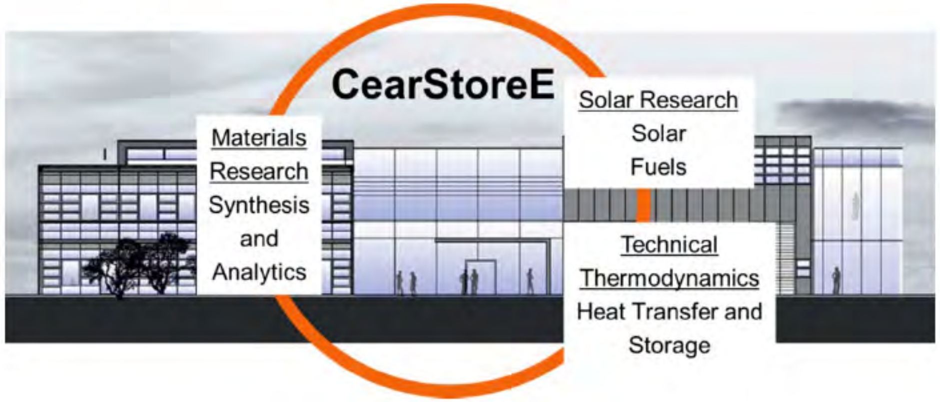
Solar Chemical Engineering
Dr. C. Sattler (26 P)

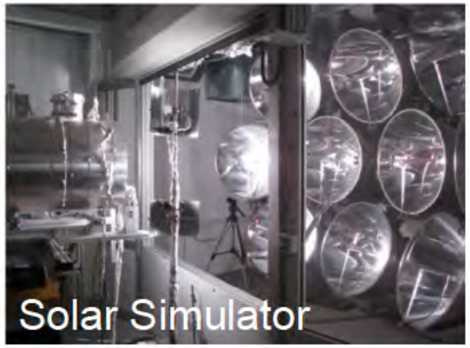
Facilities and Solar Materials
Dr. K.-H. Funken (20 P)

DLR

Large scale facilities





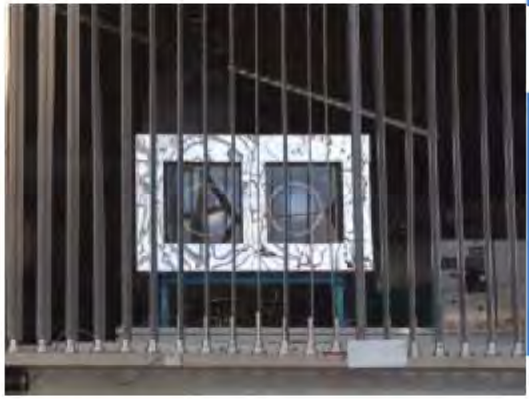


Department of Solar Chemical Engineering

Head
Organisation
Strategy
Representation in boards

Group
High temperature CE
Solar tower >500°C

Group
Low temperature CE
Reactors up to Parabolic troughs < 500°C



Solar Fuels
Solar Materials

Heat transfer fluids
Solar fuels
Water treatment
SOWΛRLΛ GmbH

27 Co-workers from Brazil, Canada, France, Germany, Greece, India, Ireland, Italy, Mexico, Tunesia and the USA + 10 Grad-Students, 65% external funding

DLR-DAAD PhD, and Post-Doc Program

DLR

Technical Optimization in all Dimensions necessary

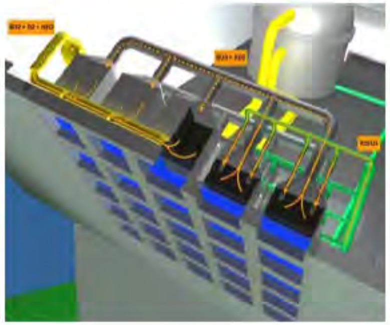
$10^4 - 10^2$ m
Solar Plant

Site

Solar field

Simulation

Environmental impact



$10^2 - 10^1$m
Receiver

Design

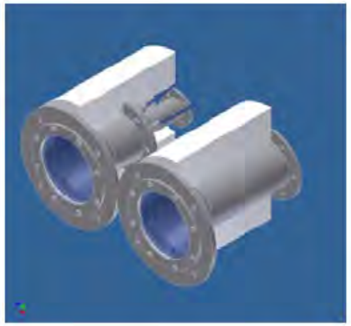
Simulation

Construction

Testing

Next-Generation-

Development



$10^1 - 10^{-2}$m
Receiver-
components

Materials

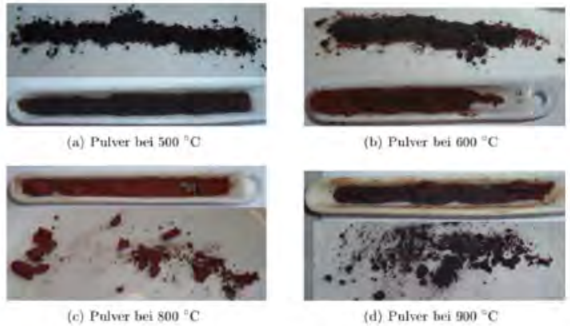
Design

Heat and

Mass transport

Simulation

Testing and Develpment



$10^{-2} - 10^{-8}$ m
Reactive Systems

Simulation

Synthesis

Chemical Charactristics

Physical Characteristics

DLR

High Temperature Group

Theoretical work
- Understanding of phenomena
- Modelling

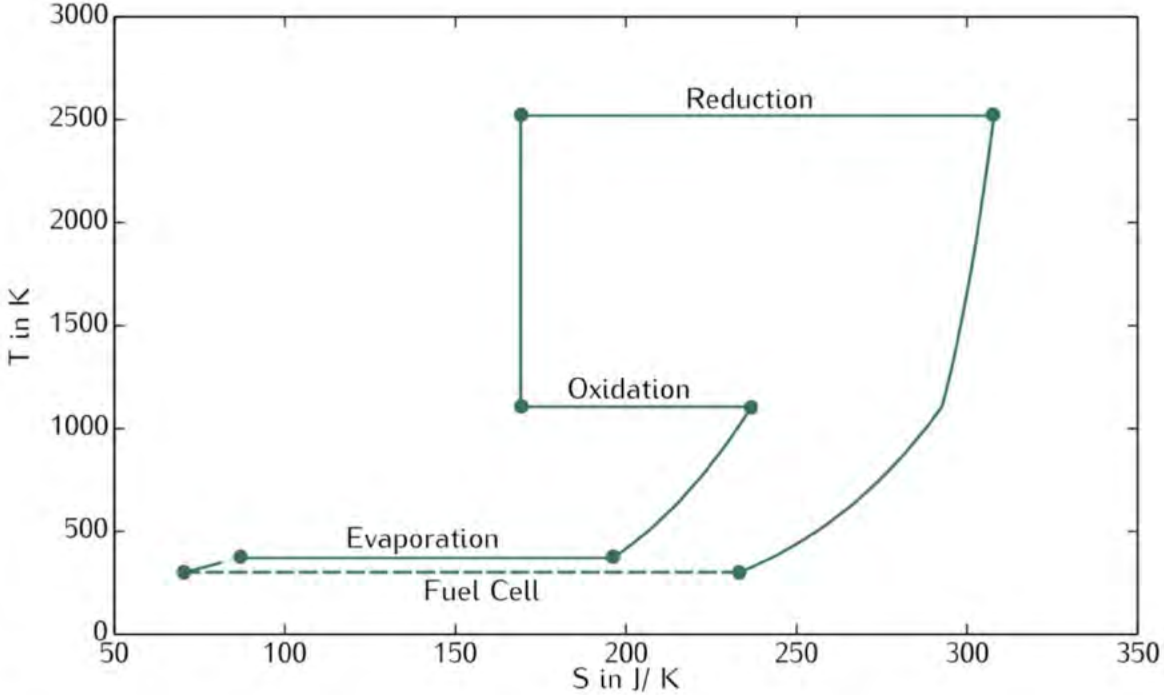
Scientific work
- Lab experiments
- Materials development
- Validation of theories and models

Engineering work
- Reactor development and testing
- Scale-up
- Process development

Techno-economic work
- Flow-sheeting
- Techno-economic evaluation
- Political consulting

T-S diagram of two-step thermochemical cycle to split 1 mol of water

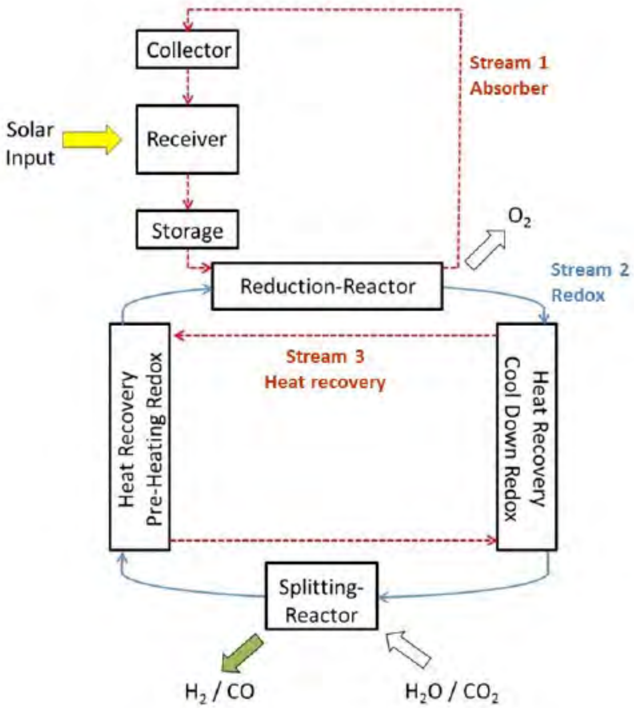
- Analyzing the thermodynamics
- Entropy change in the gas phase
- The integral of the closed curve is equivalent to the Gibbs energy of reaction of one mole of hydrogen with oxygen.
- When reducing the oxygen partial pressure during reduction, the area can be enlarged on the right side, providing the possibility to reduce the upper reaction temperature

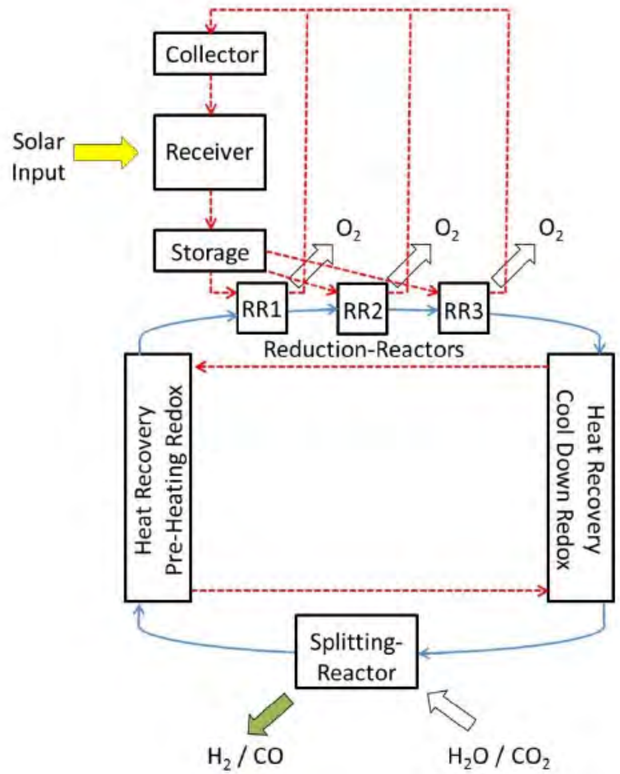


M. Lange, M. Roeb, C. Sattler, R. Pitz-Paal (2014) Energy, 67, 298-308. DOI: 10.1016/j.energy.2014.01.112

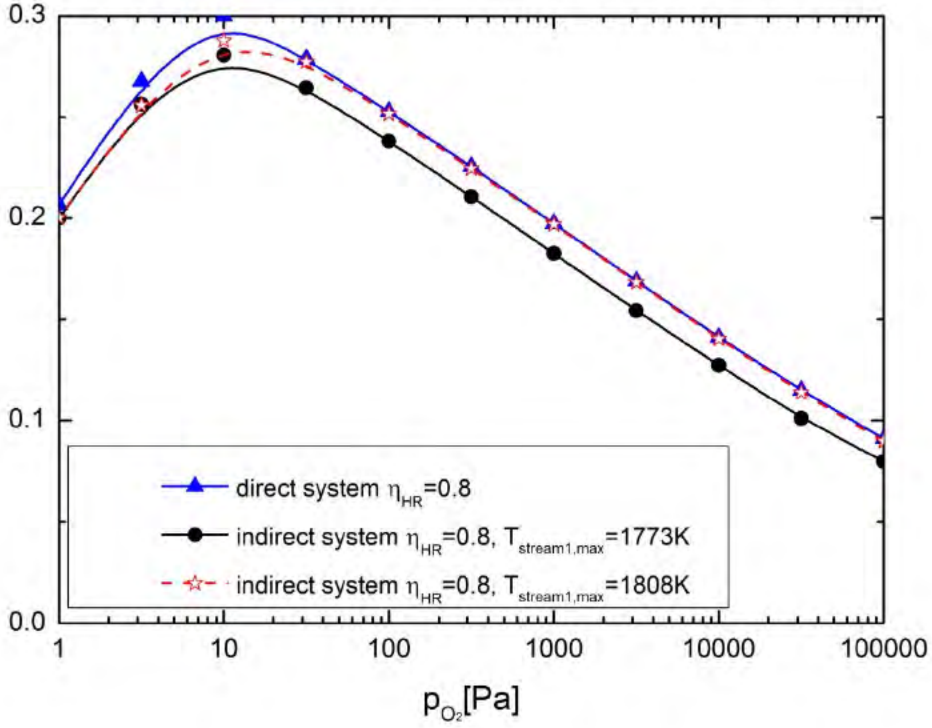
Indirect solar driven thermo-chemical redox concept

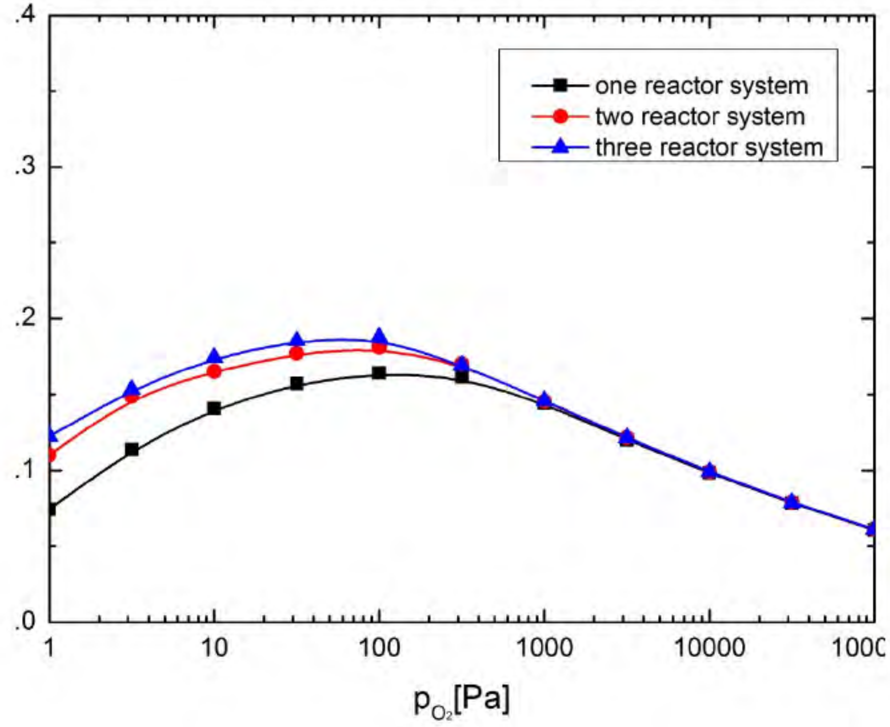
- Brendelberger ASME, Solar Energy





Efficiency evaluation of the ceria redox cycle using solar reactors

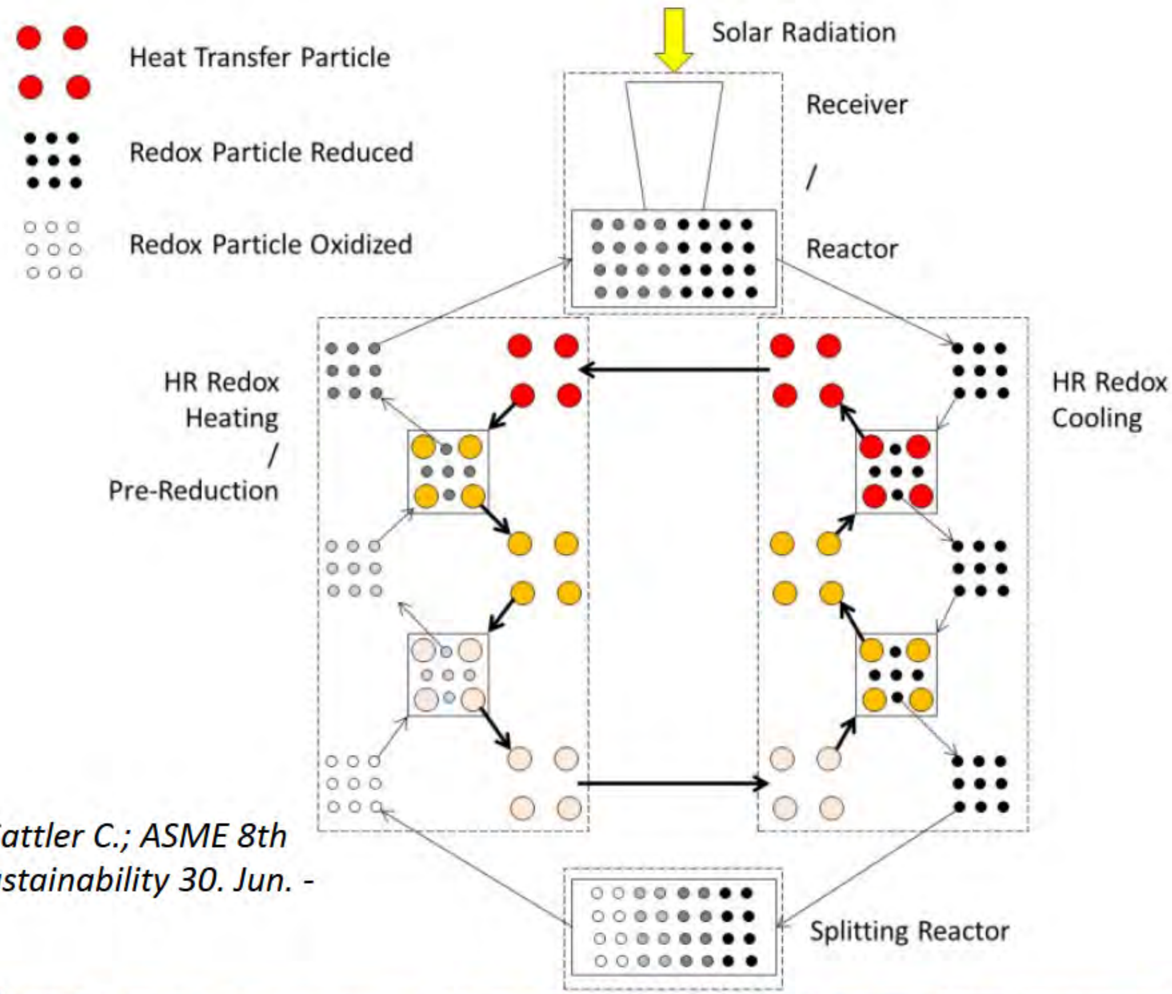




Brendelberger S., Sattler C., (2015) Solar Energy, 113, 158-170; DOI: 10.1016/j.solener.2014.12.035.

Solid phase heat recovery and multi chamber reduction for redox cycles

- Receiver - Reactor for the irradiation of the redox material
- Two heat recovery sections for the cooling and pre-heating of the redox material using a particulate heat transfer medium
- Splitting reactor for the splitting of H_2O or CO_2 using reduced redox material



Brendelberger S., Felinks J., Roeb M., Sattler C.; ASME 8th International Conference on Energy Sustainability 30. Jun. - 02. Jul. 2014, Boston, MA, USA.

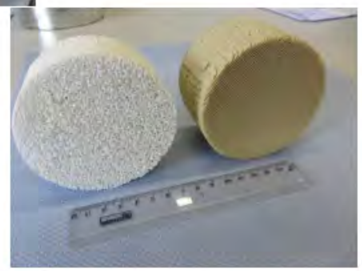
DLR

Scale evolution

TGA

Lab-scale furnace test rig

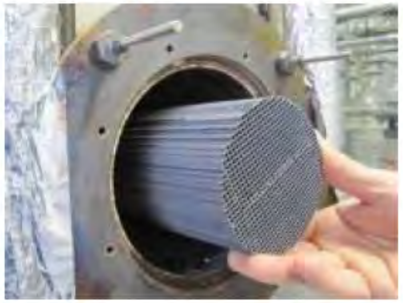
Solar receivers



DLR

Comparative testing of three SiC receivers (190 slm)

SiSiC honeycomb
90 cpsi; Schunk
Weight ≈1404 g
Length = 15 cm

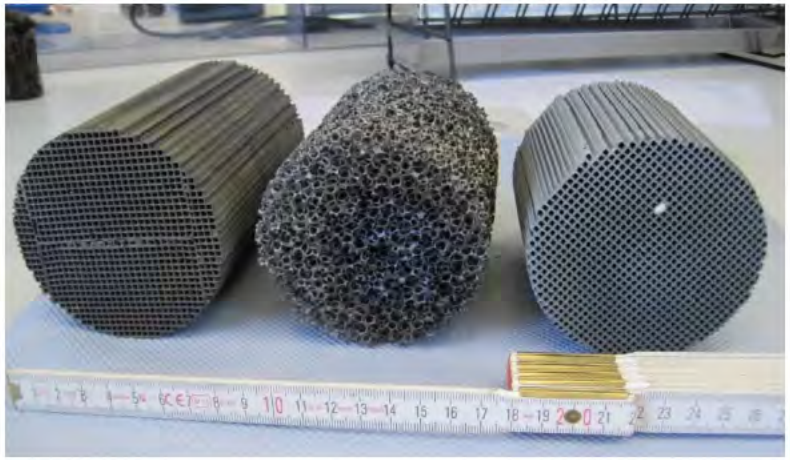


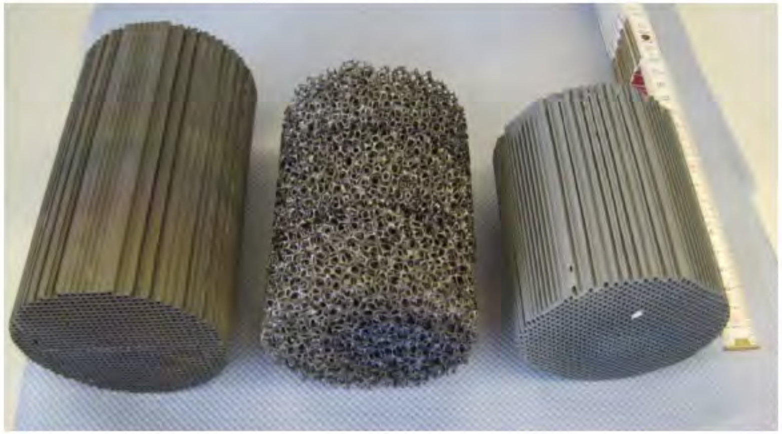
3 SiSiC foams
10 ppi; ERBICOL
Weight ≈ 246 g
Length = 12 cm

ReSiC honeycomb
90 cpsi; Stobbe TC
Weight ≈ 584 g
Length = 10 cm

Rationale for using ReSiC

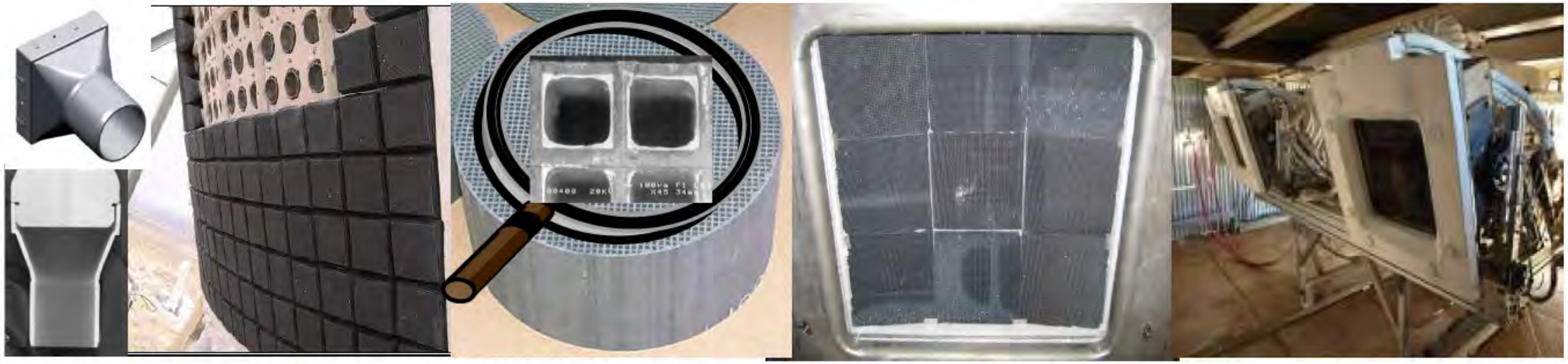
- Possibility to exceed 1370ºC on the front irradiated surface (m.p. > 2000ºC).
- Temperature measurement with an IR camera ("matched" to TC1 indication for T < 1370ºC).





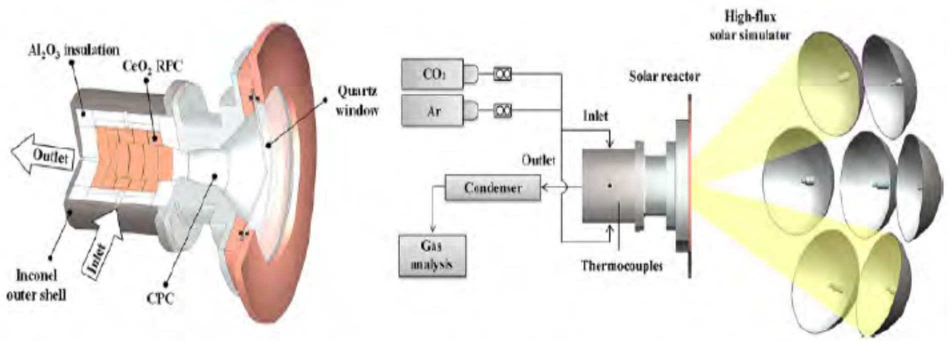
DLR

Solar Receiver Components and reactive Systems



C. Agrafiotis, M. Roeb, A.G. Konstandopoulos, L. Nalbandian, V.T. Zaspalis, C. Sattler, P. Stobbe, A.M. Steele, Solar water splitting for hydrogen production with monolithic reactor, Solar Energy, 79(4), 409-421, (2005).

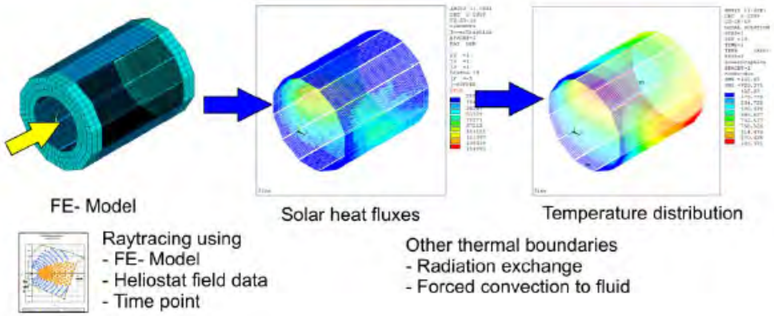
Reactive coated structures and structures made from reactive materials



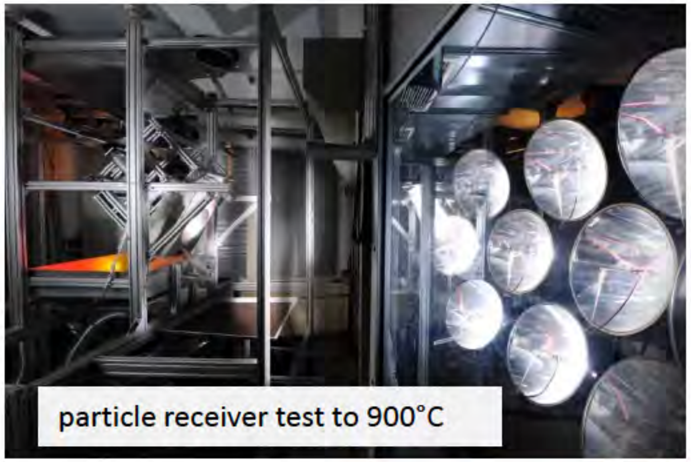
P. Furler, J. Scheffe, M.Gorbar, L. Moes, U. Vogt, A. Steinfeld, Solar Thermochemical CO_2 Splitting Utilizing a Reticulated Porous Ceria Redox System, Energy & Fuels, 26(11), 7051-59, (2012).

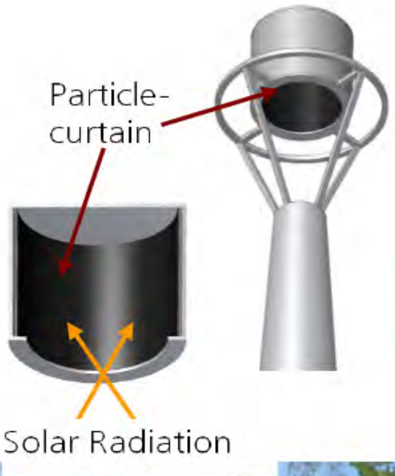
Receiver Technology R&D

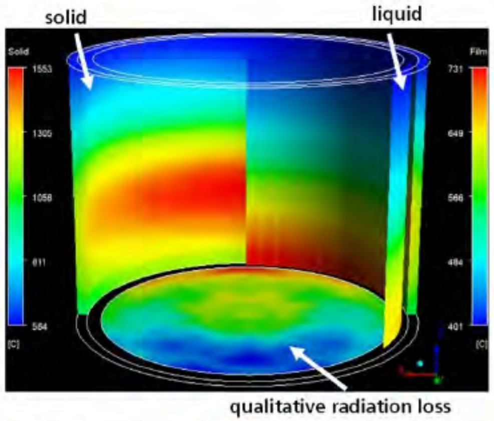
- development / technology transfer
    - open volumetric air receivers
    - pressurized air receivers



- extension to liquid heat transfer media
    - e. g. molten salt
- innovative concepts: direct absorption receivers



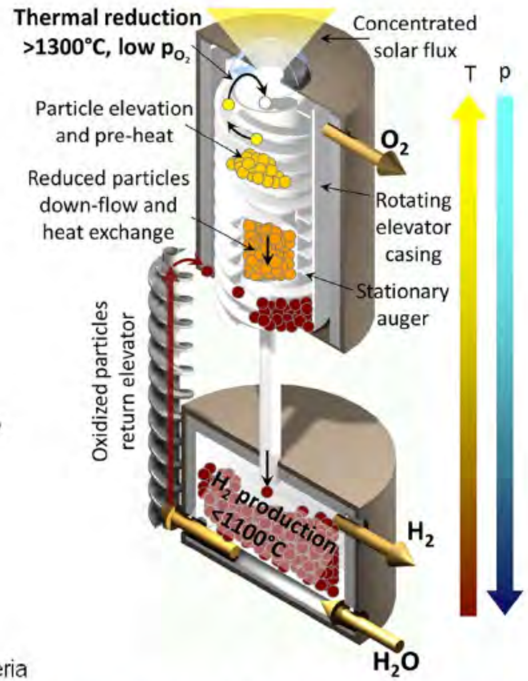


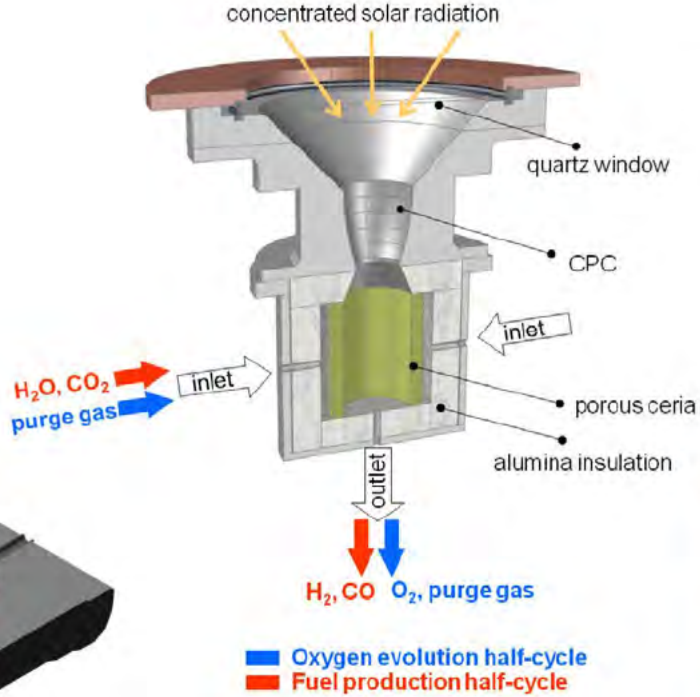


Receiver – Concepts for Solar Chemistry

- Challenges:
  - Temperature
  - Corrosion
  - Abrasion
  - Process operation

- Goals:
  - Efficiency
  - Durability
  - Cost





German Project
Solar heated rotary kiln, DLR

European Project
Solar heated Cavity-Gas Receiver with porous Ceramic structur
A. Steinfeld et al., ETH Zürich

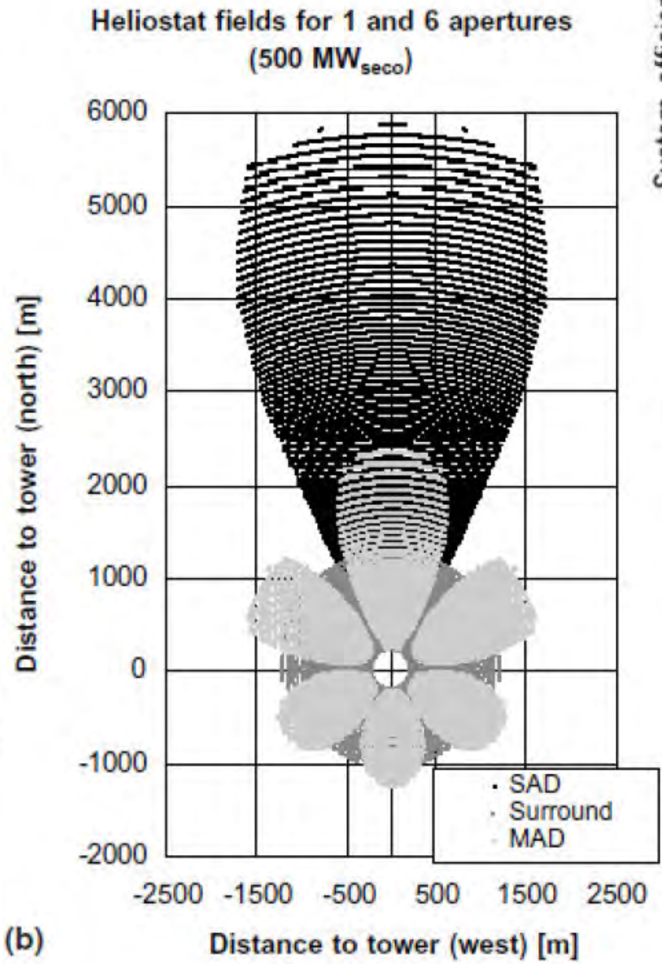
DoE Project with DLR participation
Solar heated Partikel-Receiver
I. Ermanoski et al., Sandia Natl. Lab.

DLR

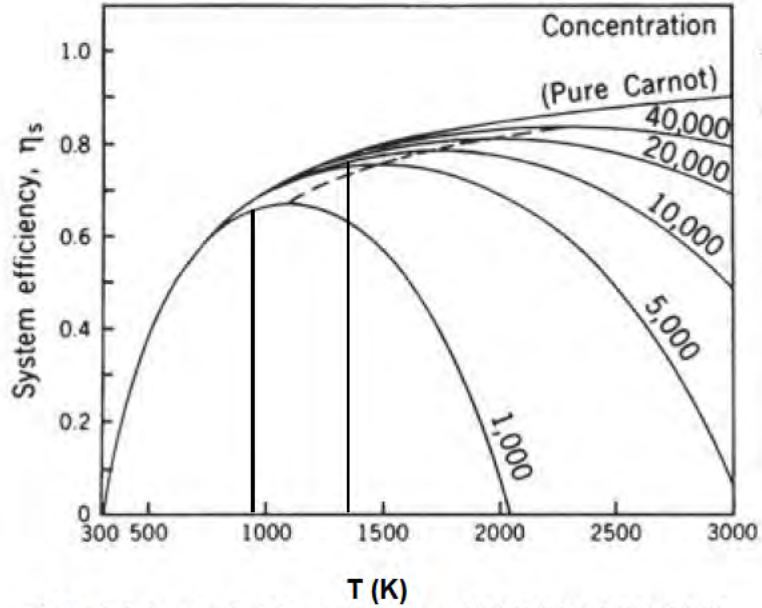
Solar Field Development

The field has to be designed for its application:

- Location
- Concentration ratio to achieve the Process temperature
- At high concentration (1000 suns) secondary optics have to be taken into account



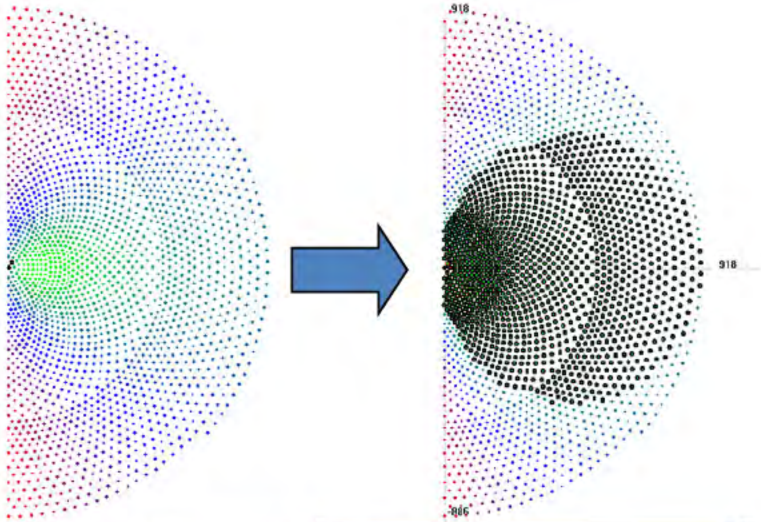
M. Schmitz et al., Solar Energy 80 (2006) 111–120.



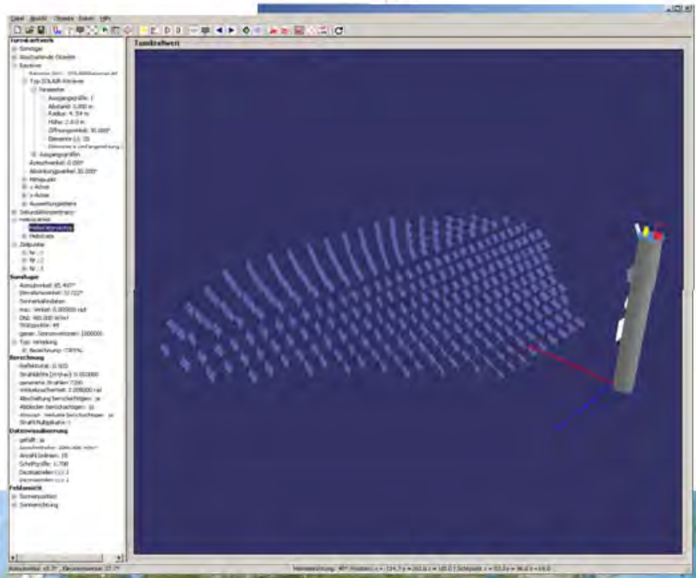
E.A. Fletcher, R.L. Moen, Science, 197 (1977) 1050-1056.

Simulation Tool Development
for Solar Tower Systems

- heliostat field layout



- performance simulation
  - flux distribution
  - aim point strategy
  - efficiency



DLR

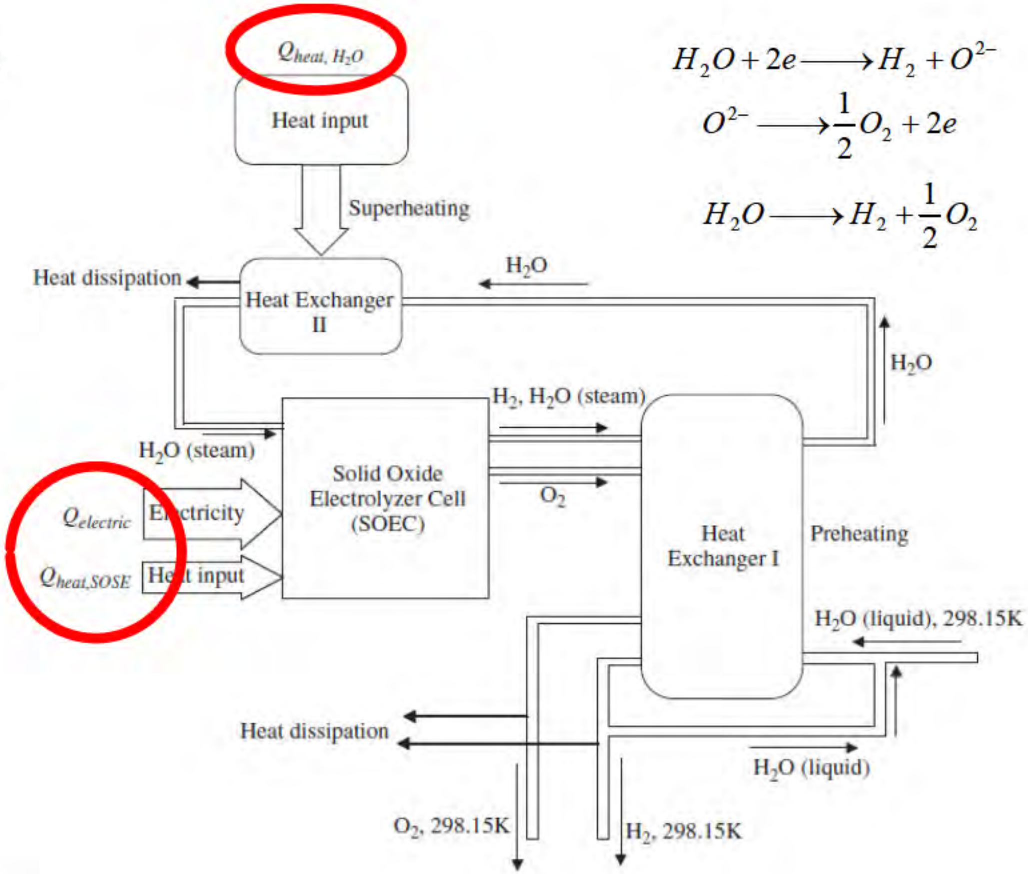
High temperature electrolysis process

- Temperature in the range of 600°C to 900°C are required to drive the electrolyser.
- Electricity and heat are supplied to the electrolyser to drive the electro-chemicals reactions.
- The waste heat from the H_2 and O_2 gas streams existing the cell is used to evaporate water.
- The H_2O stream is further heated by the second Heat exchanger to raise the temperature of the electrolyser.

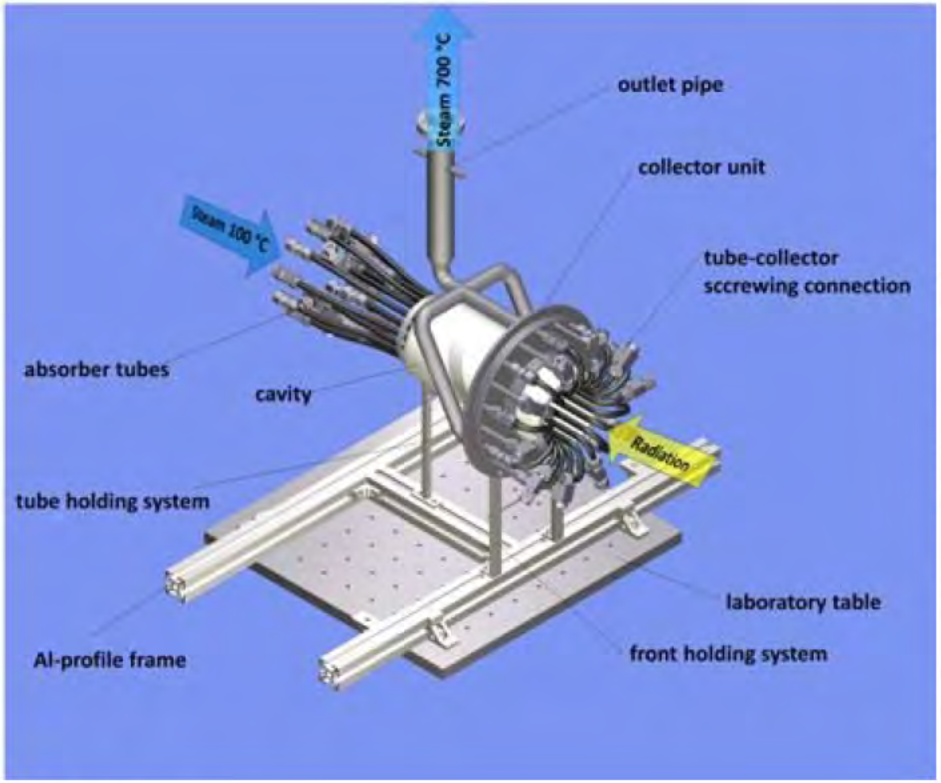
$$H_2O + 2e \longrightarrow H_2 + O^{2-}$$

$$O^{2-} \longrightarrow \frac{1}{2}O_2 + 2e$$

$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$$



Solar Superheated Steam Generator for SOEC

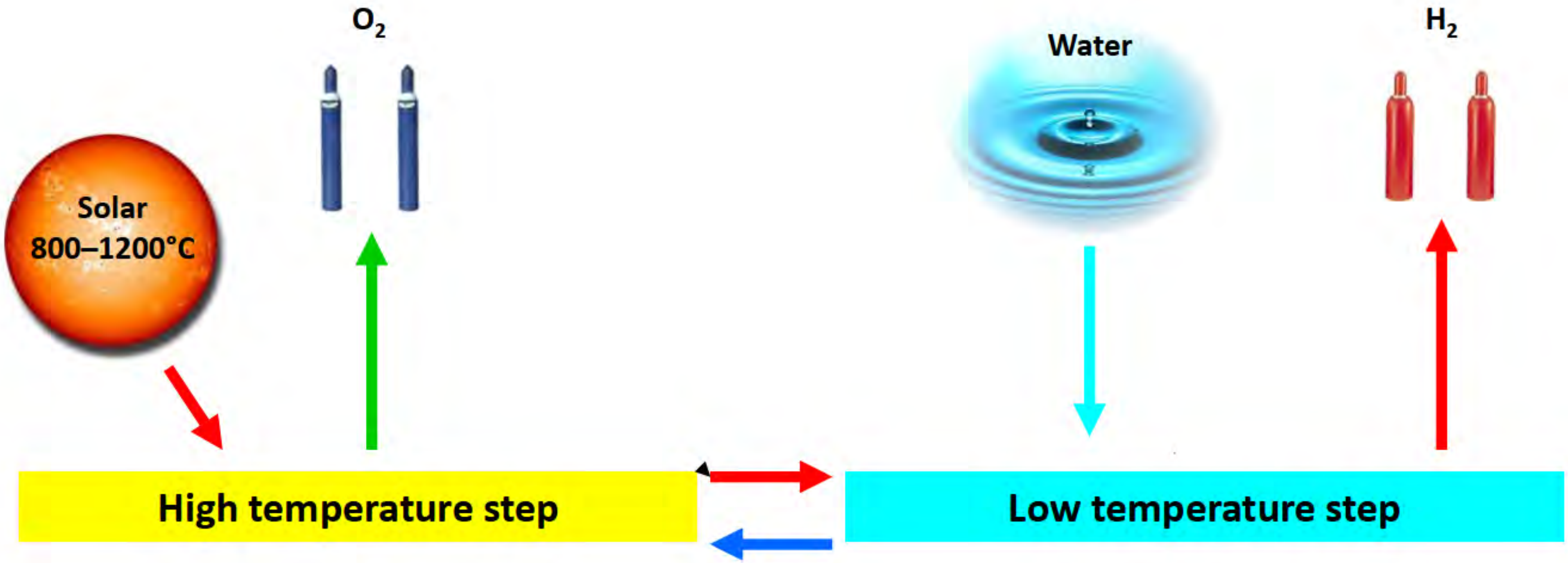


3D Design

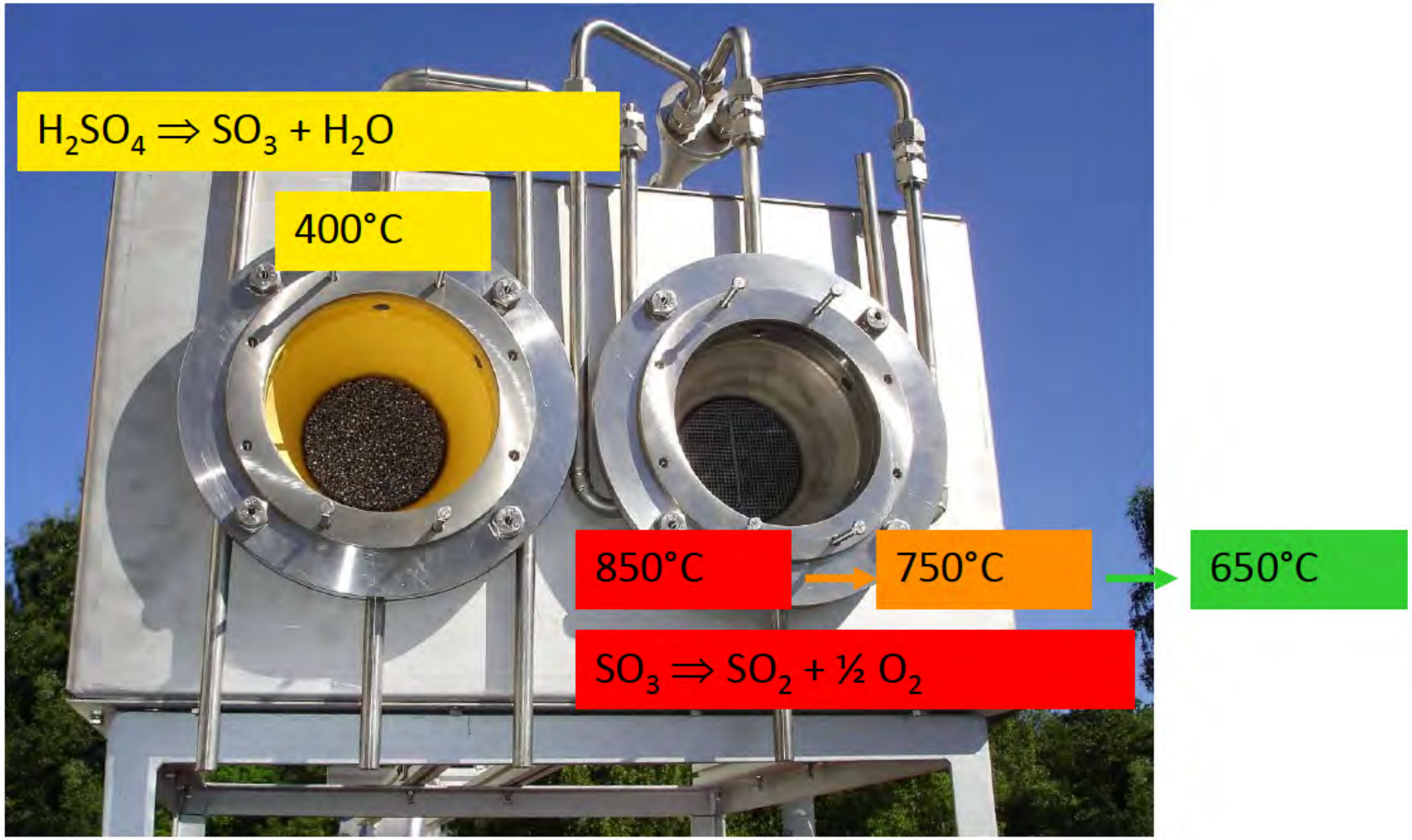
Operation in the solar simulator providing 5 kg/h steam at 700 °C

http://www.sophia-project.eu/

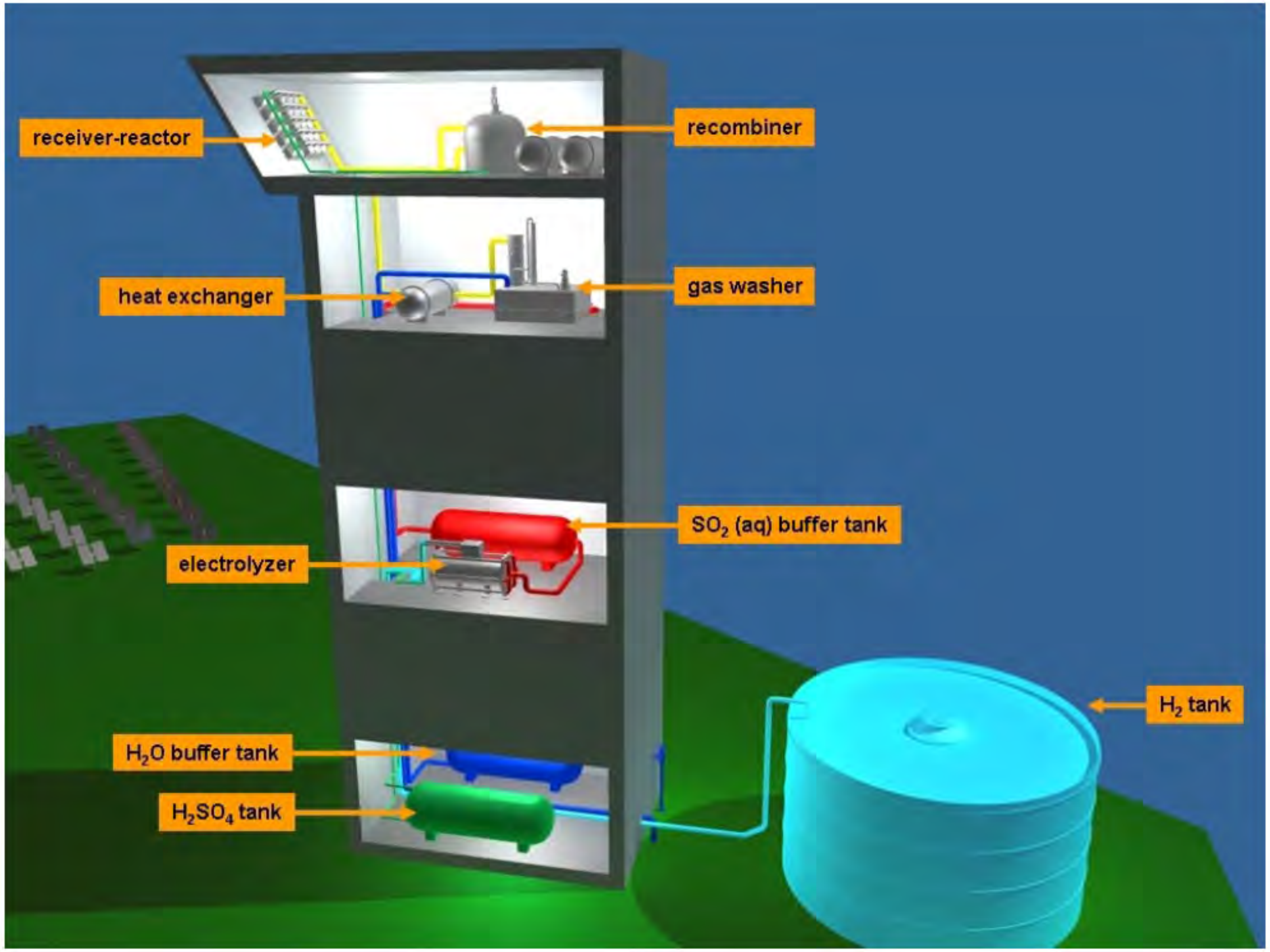
Hybrid Sulfur Cycle (HyS, Westinghouse)



Solar reactor for sulfuric acid decomposition



Implementation into a Solar Tower

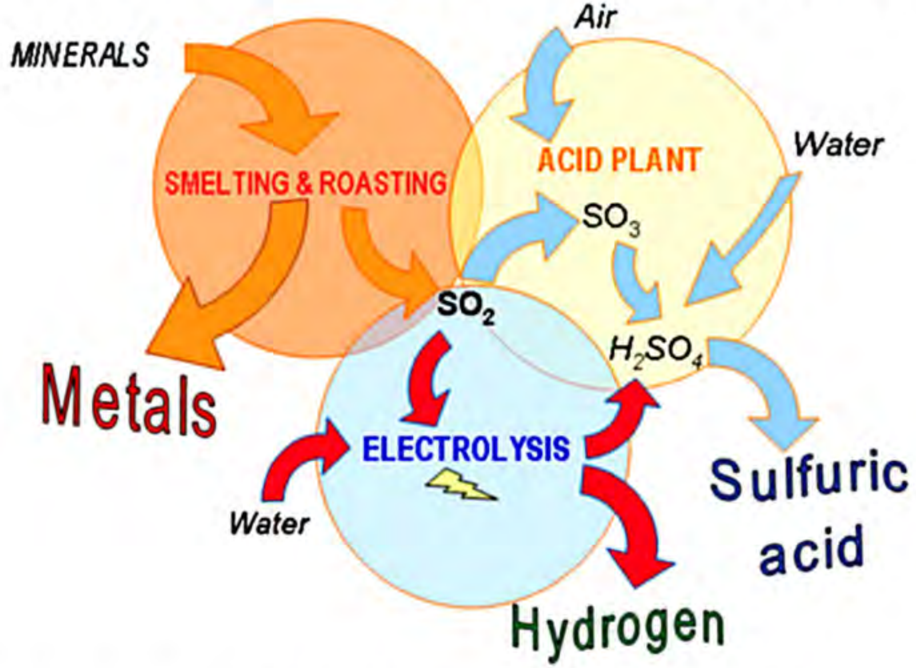


SOL2HY2 – Solar To Hydrogen Hybrid Cycles

- FCH JU project on the solar driven Utilization of waste SO_2 from fossil sources for co-production of hydrogen and sulphuric acid
- Hybridization by usage of renewable energy for electrolysis
- Partners: EngineSoft (IT), Aalto University (FI), DLR (DE), ENEA (IT), Outotec (FI), Erbicol (CH), Oy Woikoski (FI)
- >300 kW demonstration plant on the solar tower in Jülich, Germany in 2015

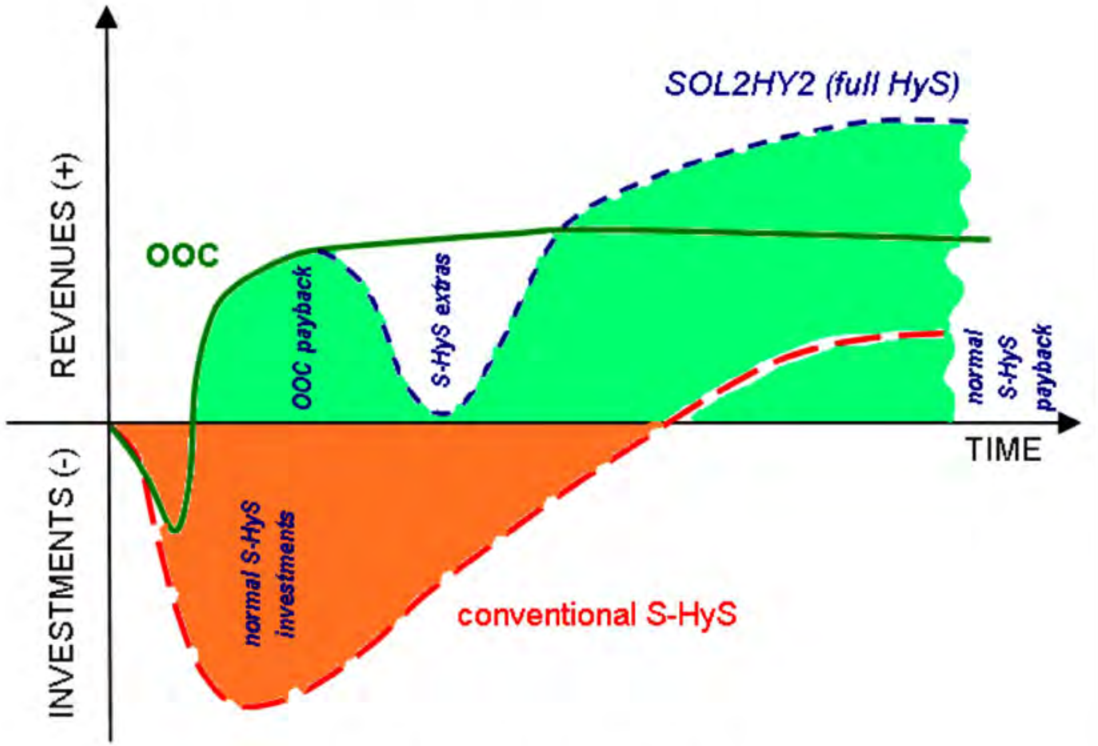
https://sol2hy2.eurocoord.com

Outotec™ Open Cycle (OOC)



- Utilization of waste SO_2 from fossil sources
- Co-production of hydrogen and sulphuric acid
- Hybridization by renewable energy for electrolysis

Investments vs. revenues

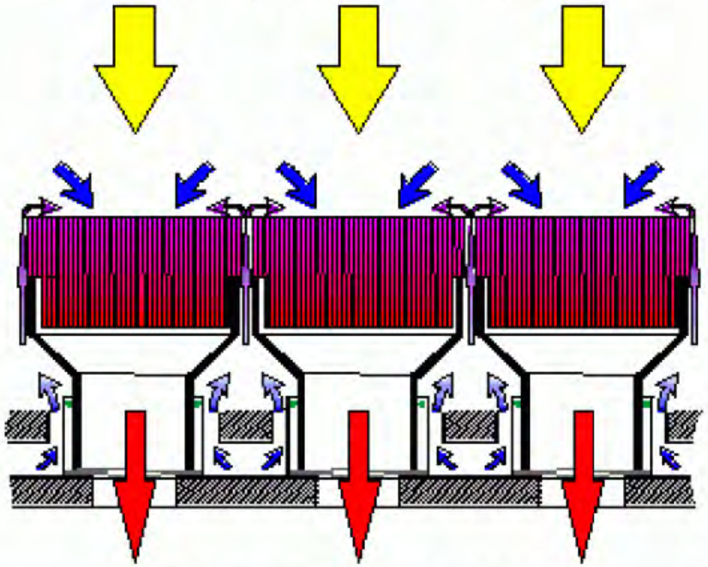


- Reduction of initial investments
- Financing of HyS development by payback of OOC
- Increase of total revenues

The HYDROSOL Idea

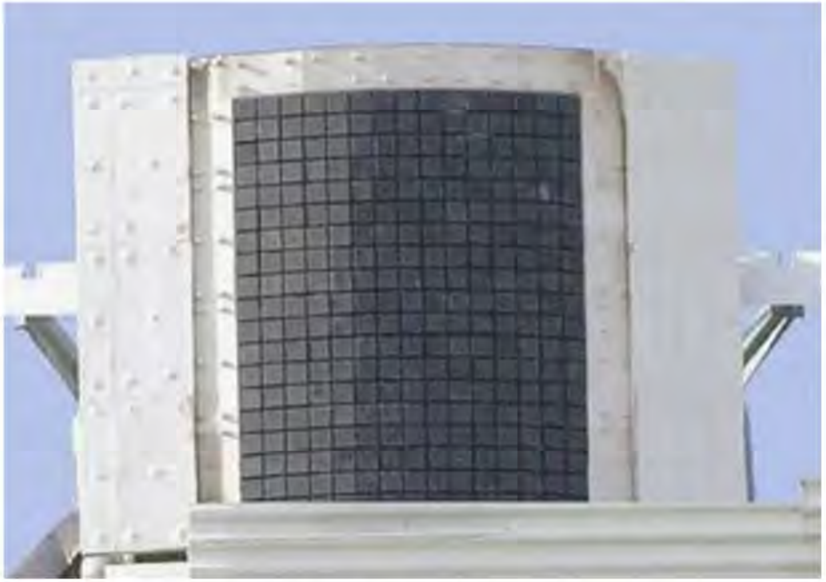
2001, Almería, Spain – Discussion between APTL and DLR
Open Volumetric Solar Receiver Design: High Temperature Air Receiver (HiTRec)

Volumetric receiver concept
SiSiC monoliths with
Honey comb structure



Hot Air 760 – 1000°C

- PSA Demonstration:
  Power: 3 MW_{th}



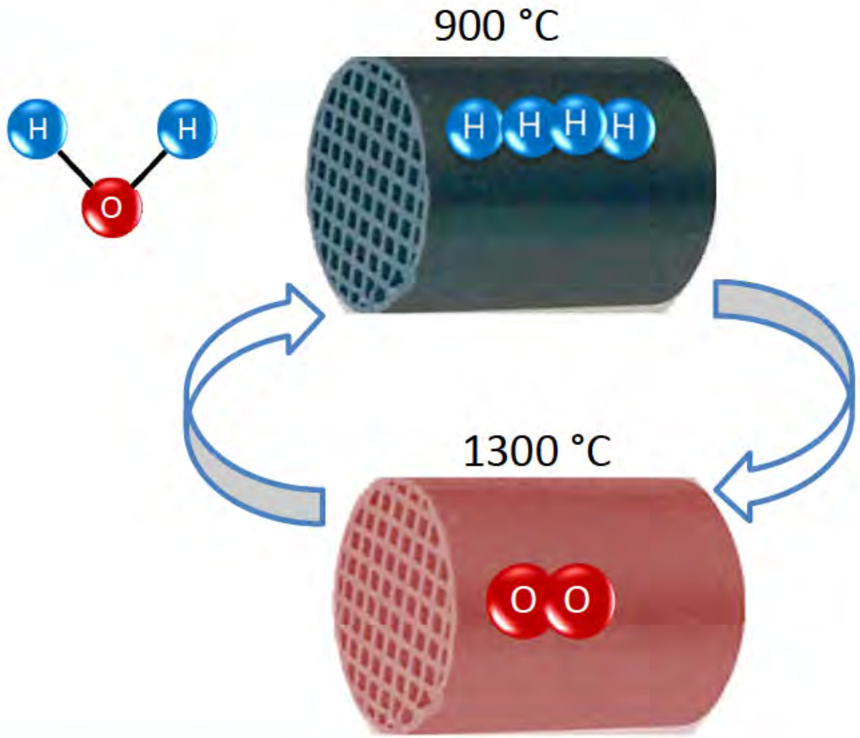
- Irradiation > 750 kW/m^2
- Long term test at PSA

Result: HYDROSOL Project - STREP EU FP 5 (Nov. 2002 – Oct. 2005)

Example how a technology is developed The HYDROSOL concept

1. Water Splitting

$H_2O + MO_{red} \rightarrow MO_{ox} + H_2$



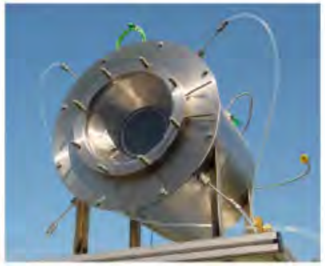
2. Regeneration

$MO_{ox} \rightarrow MO_{red} + ½ O_2$

Net Reaction: $H_2O \rightarrow H_2 + ½ O_2$

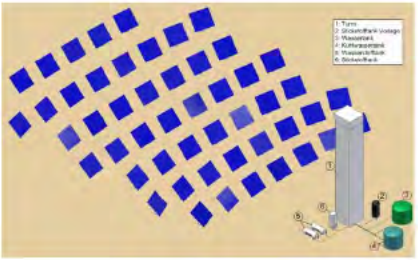
HYDROSOL Development

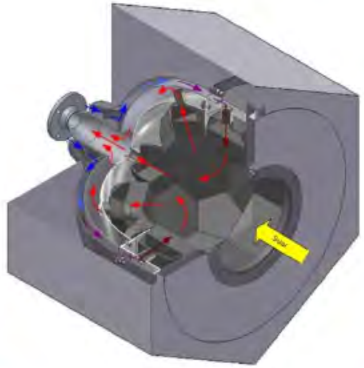
Hydrosol I
2002 – 2005
< 10 kW



Hydrosol II
2006 – 2009
100 kW

Hydrosol 3D
2010 – 2012
1 MW



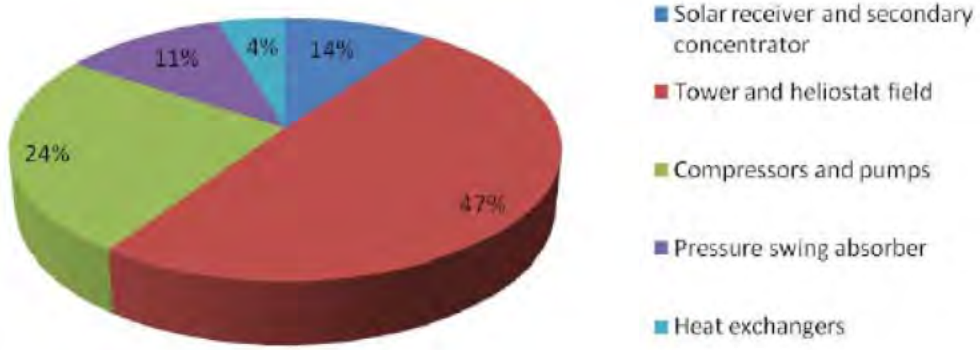


Solar fuels from thermochemical cycles- HYDROSOL 3D project- Main results Economic analysis of the demonstration plant

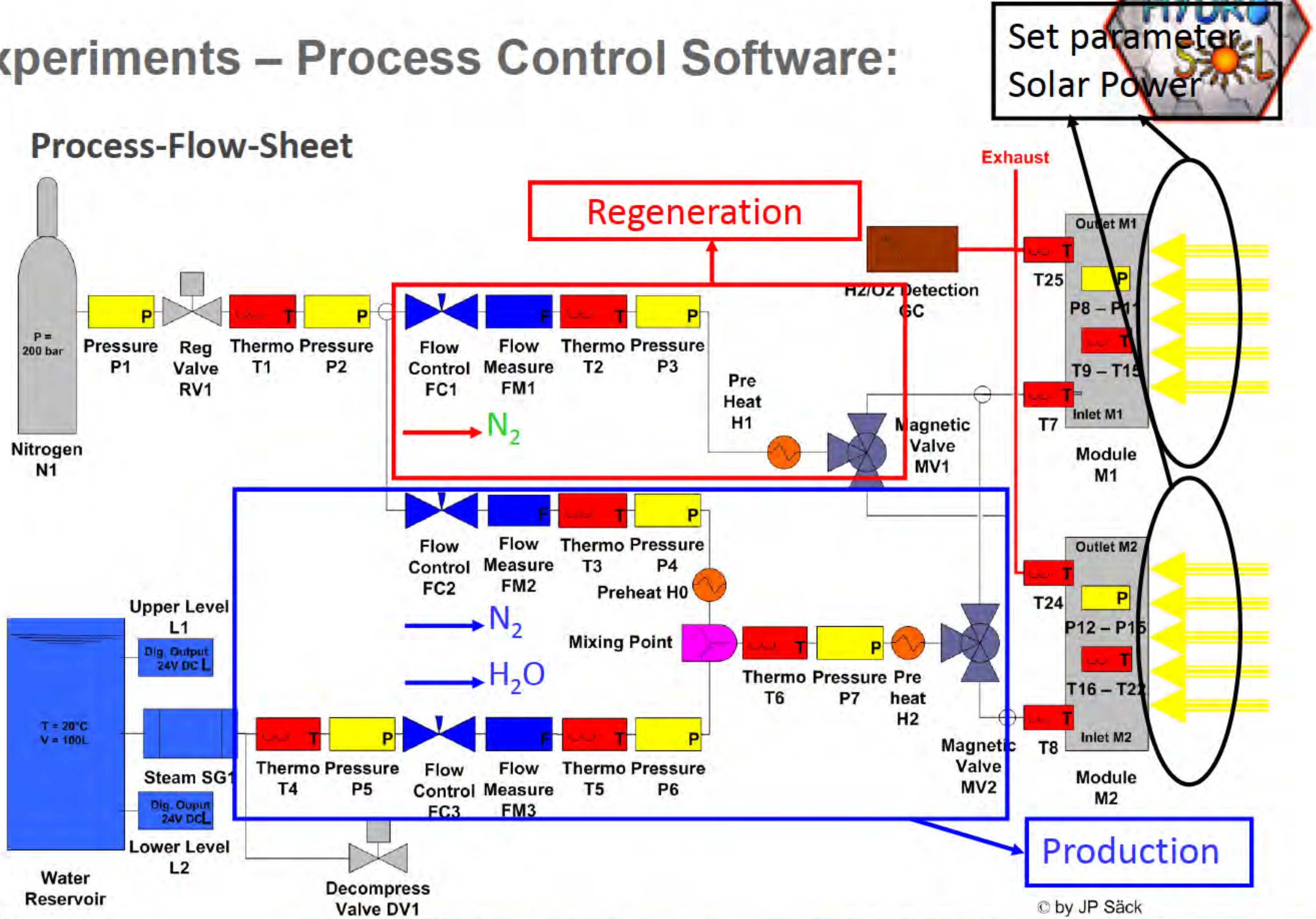
- Demonstration plant thermal energy input: 1 MW
- Cost calculation of the new designed reactor was carried out.
- Cost calculation of the overall process units was performed.
- More than half of process investment results from the solar system.

Component	Number of units	Cost per unit [€]	Total Cost [€]
Quartz plates	14	600	8400
Reactor modules	14	3000	42000
Secondary concentrator	14	12000	168000

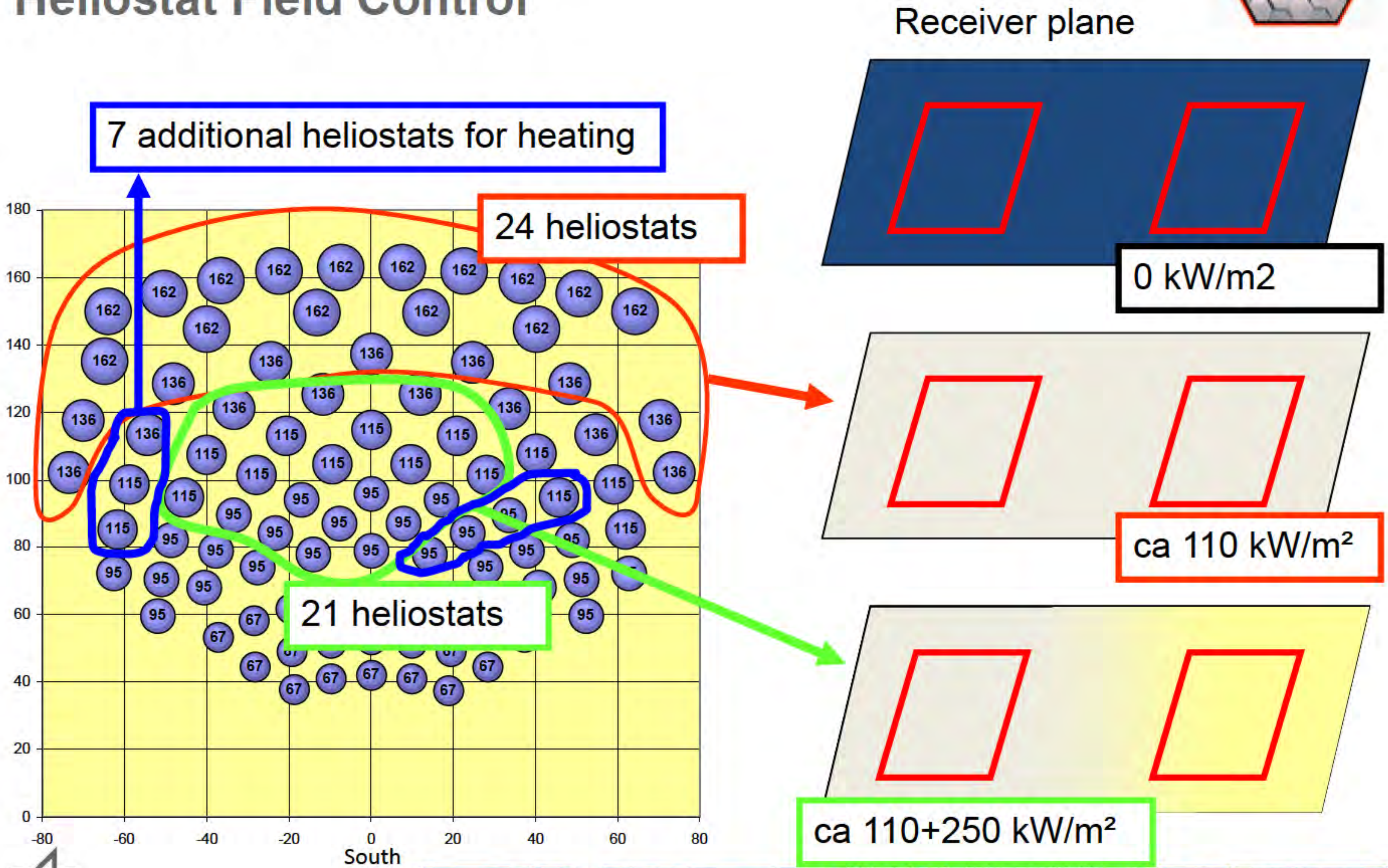
Solar part incl. receiver-reactor[€]	1,406,847
Pressure swing absorber [€]	265,000
Compressors and pumps [€]	584,054
Heat exchangers [€]	110,493
Total cost [Mio. €]	**2.366**



Experiments – Process Control Software:

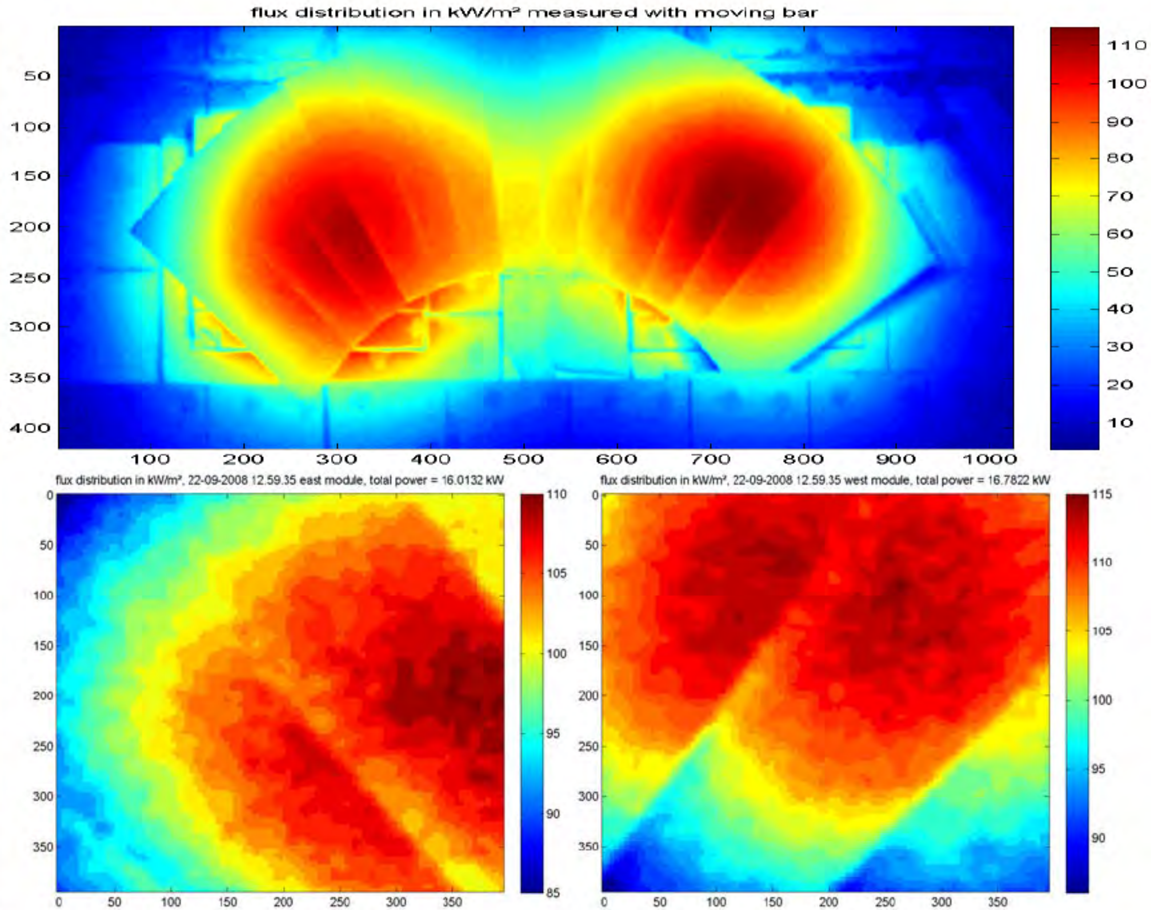


Heliostat Field Control



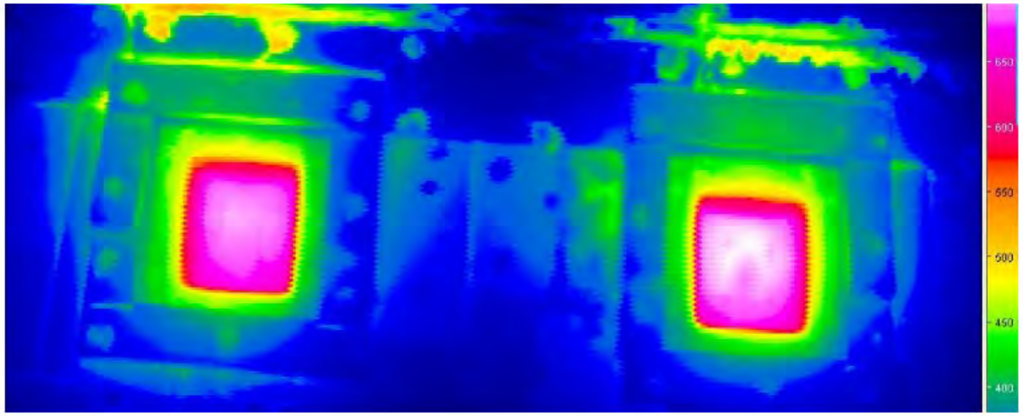
Experiments – Process Control Software:

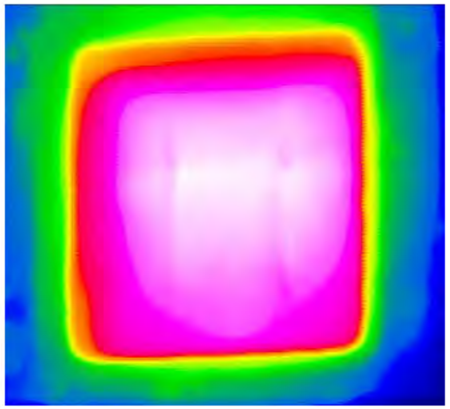
Flux Measurement at test operation $\text{Flux}_{\text{Max}_{\text{both Modules}}} = 115 \text{kW/m}^2$

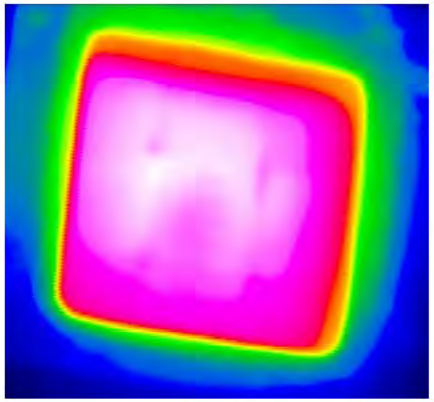


Experiments – Process Control Software:

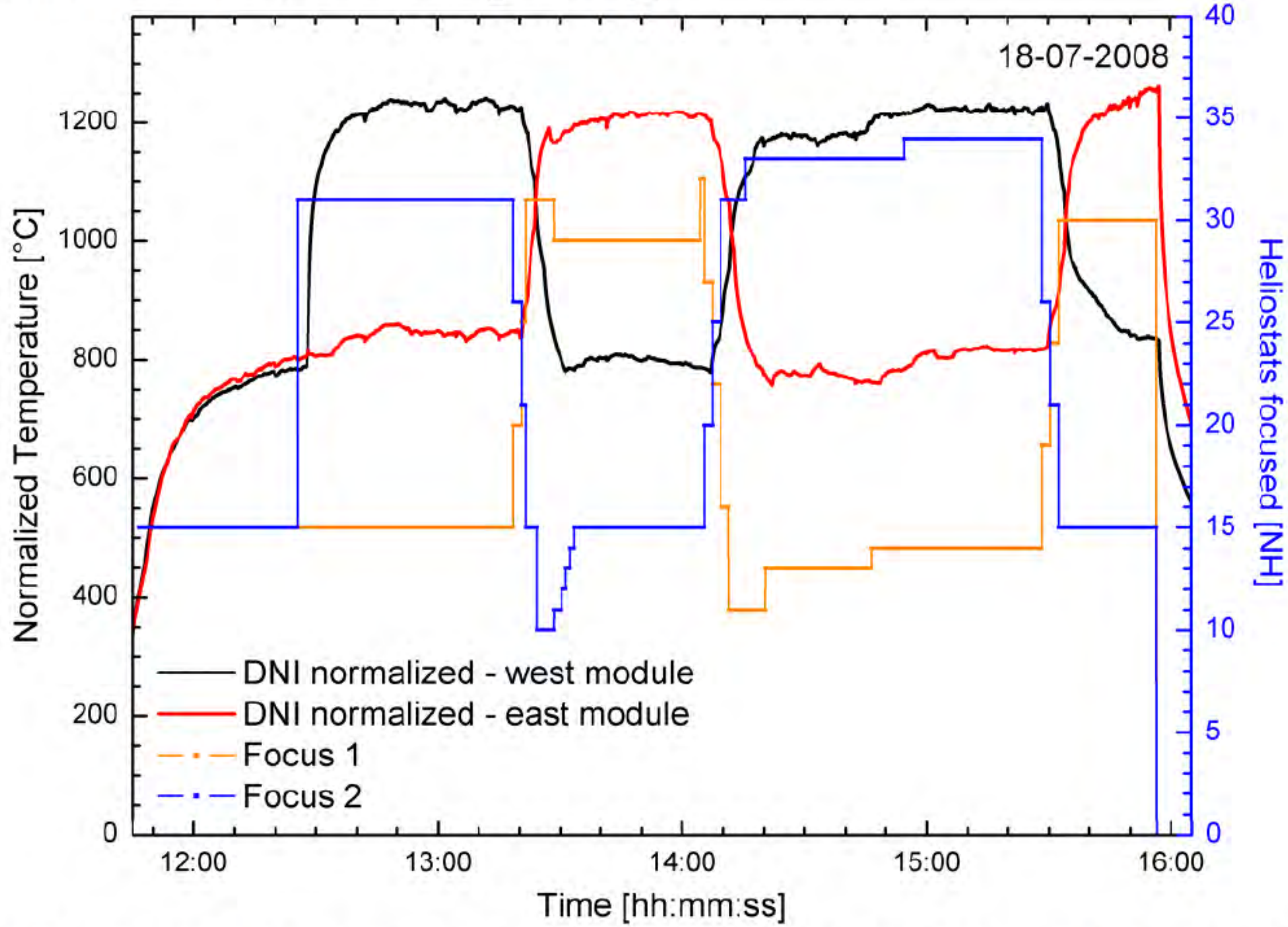
Temperature measurement at test operation $T_{Max_{both\ Modules}} = 800°C$







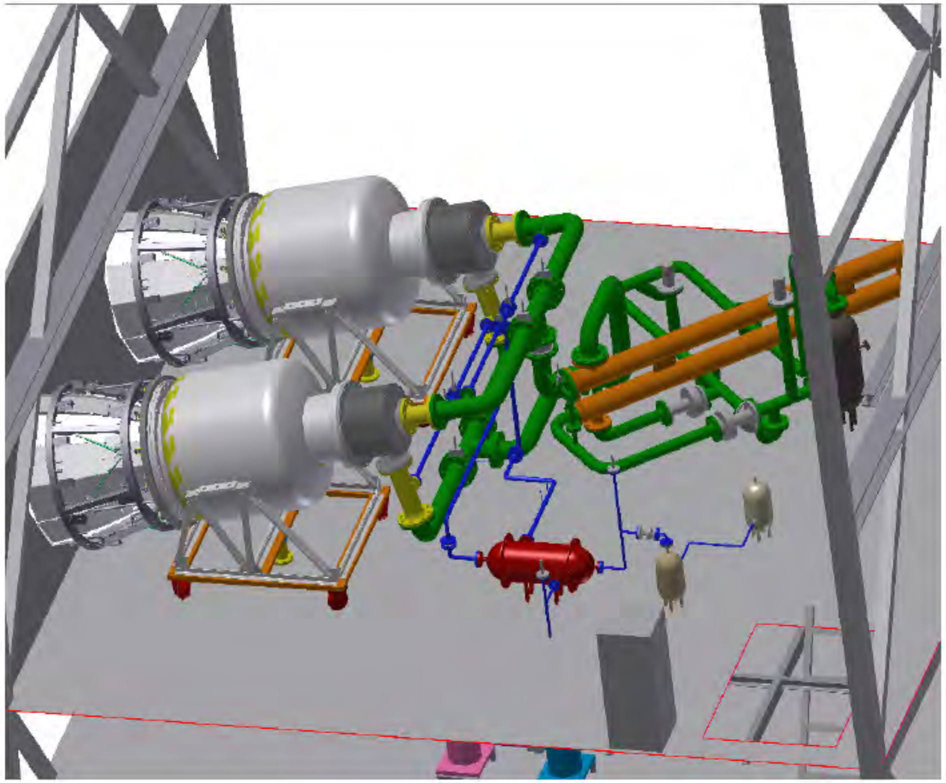
Results: Thermal cycling



Säck J.-P., Roeb M., Sattler C., Pitz-Paal R., Heinzel A. (2015) Solar Energy, 112 (2), 205-217.
DOI: 10.1016/j.solener.2014.11.026.

Hydrosol Plant - Design for CRS tower PSA, Spain

- European FCH-JU project
- Partner: APTL (GR), HELPE (GR), CIEMAT (ES), HYGEAR (NL)
- 750 kW_{th} demonstration of thermochemical water splitting
- Location: Plataforma Solar de Almería, Spain, 2016
- Use of all heliostats
- Reactor set-up on the CRS tower
- Storage tanks and PSA on the ground

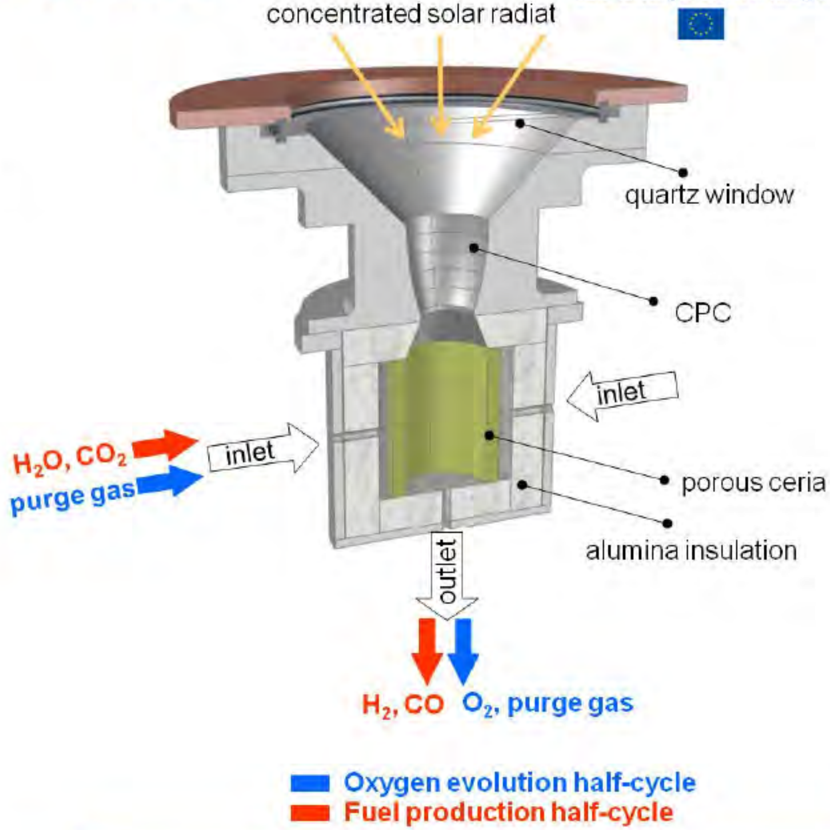


H_2O/CO_2-Splitting Thermochemical Cycles

SOLAR-JET
Zero-carbon jet fuel from sunlight

Solar Production of Jet Fuel

- EU-FP7 Project SOLAR-JET (2011-2015)
- SOLAR-JET aims to ascertain the potential for producing jet fuel from concentrated sunlight, CO_2, and water.
- SOLAR-JET will optimize a two-step solar thermochemical cycle based on ceria redox reactions to produce synthesis gas (syngas) from CO_2 and water, achieving higher solar-to-fuel energy conversion efficiency over current bio and solar fuel processes.
- **First jet fuel produced in Fischer-Tropsch (FT) unit from solar-produced syngas!**



Int. J. Heat & Fluid Flow 29, 315-326, 2008.
Materials 5, 192-209, 2012.

Partners: Bauhaus Luftfahrt (D), ETH (CH), DLR (D), SHELL (NL), ARTTIC (F)
Funding: EC

http://www.solar-jet.aero/

DLR

Steam and CO_2-Reforming of Natural Gas

Steam reforming: $H_2O + CH_4 \rightarrow 3\ H_2 + 1\ CO$

CO_2 Reforming (Dry): $CO_2 + CH_4 \rightarrow 2\ H_2 + 2\ CO$

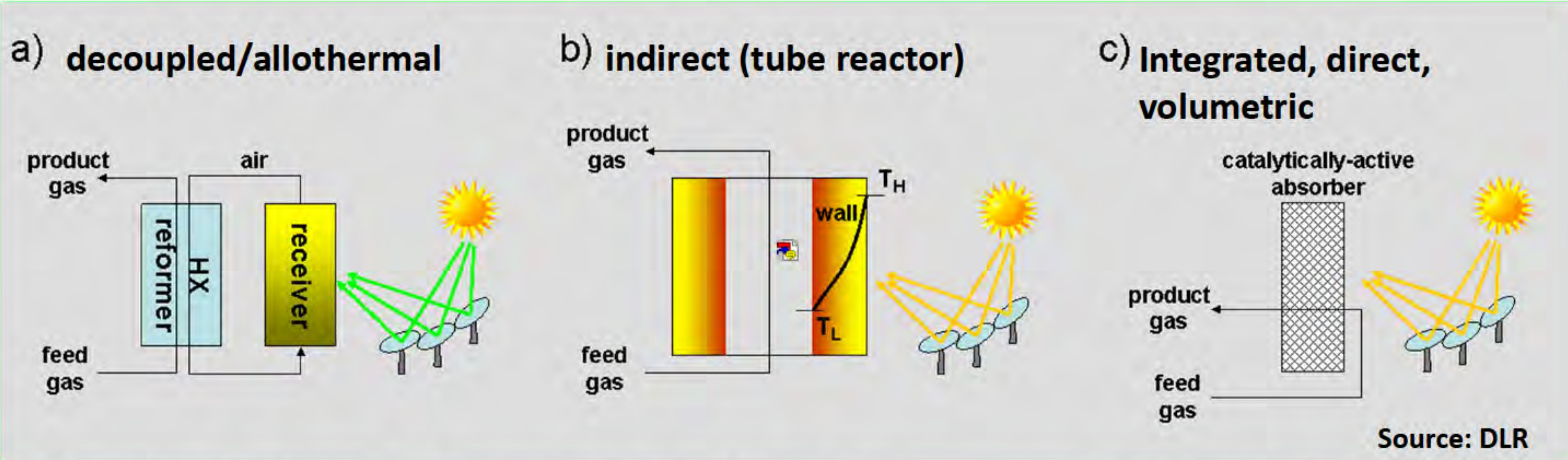
Reforming of mixtures of CO_2/H_2O is possible and common

Use of syngas for methanol production:

e.g. $2H_2 + CO \rightarrow CH_3COH$ (Methanol)

Both technologies can be driven by solar energy as shown in the projects: CAESAR, ASTERIX, SOLASYS, SOLREF…

Solar Methane Reforming – Technologies



- Reformer heated externally (700 to 850°C)
- Optional heat storage (up to 24/7)
- E.g. **ASTERIX** project

Irradiated reformer tubes (up to 850°C), temperature gradient

Approx. 70 % Reformer-h

Development: Australia, Japan; Research in Germany and Israel

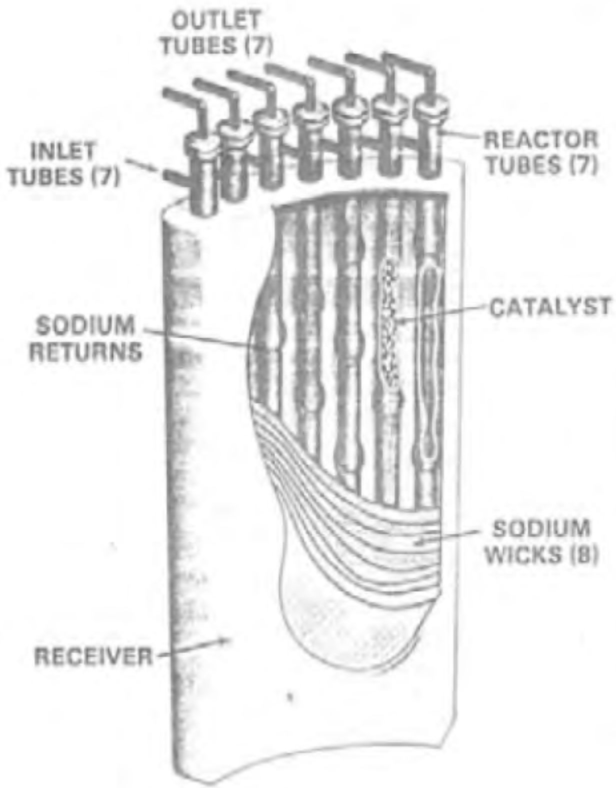
Catalytic active direct irradiated absorber

Approx. 90 % Reformer-h

High solar flux, works only by direct solar radiation

DLR coordinated projects: **SOLASYS, SOLREF**; Research in Israel, Japan

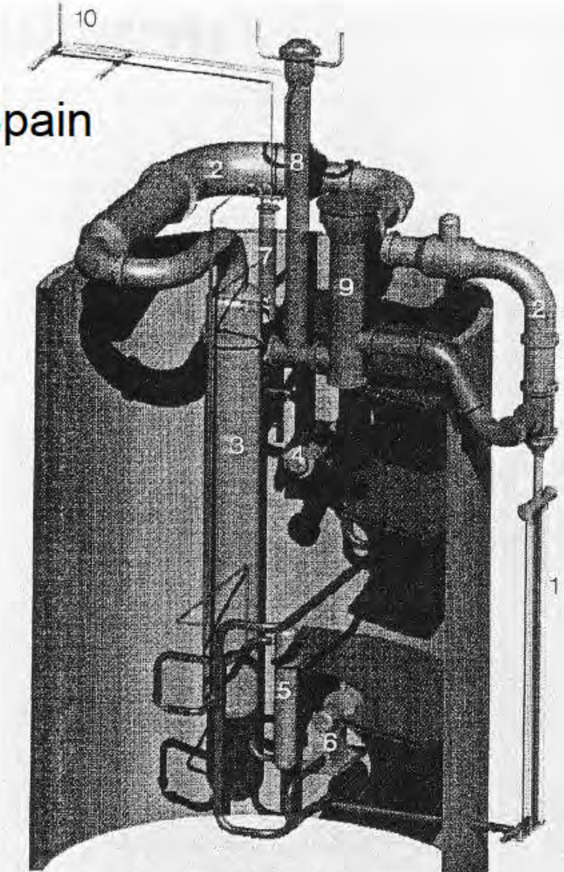
SANDIA-WIS's sodium reflux heat pipe solar receiver-reformer (1983-1984)



ASTERIX: Allothermal Steam Reforming of Methan

- DLR, Steinmüller, CIEMAT
- 180 kW plant at the Plataforma Solar de Almería, Spain (1990)
- Convective heated tube cracker as reformer
- Tubular receiver for air heating

CESA-1, PSA, Spain. The solar radiation is collected by a field of heliostats and redirected to a tower, where different platforms allow the tests of various receiver technologies.



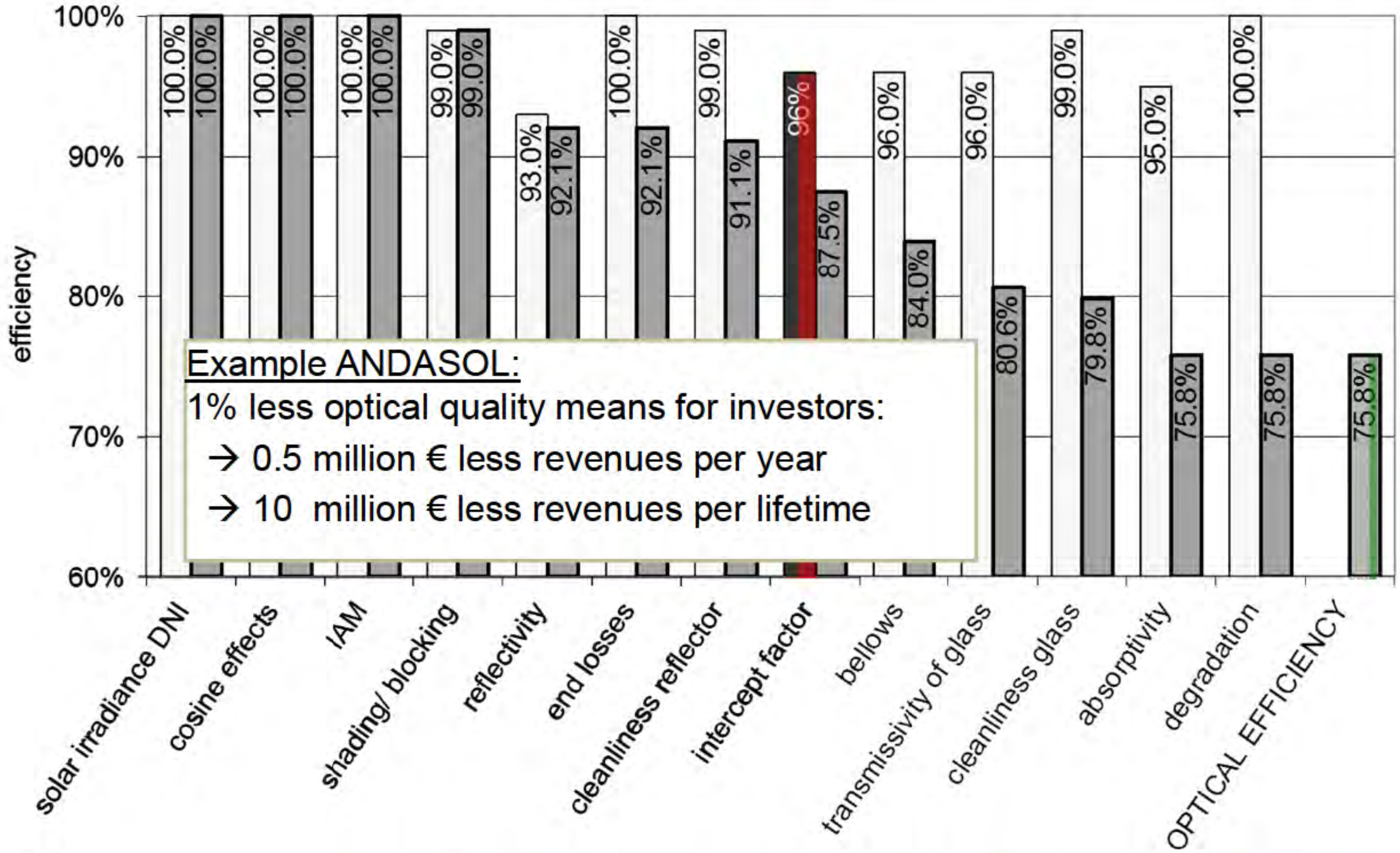
1 = Receiver, 2 = Heißgasleitungen, 3 = Rekuperator, 4 = Elektrischer Heizer, 5 = Kühler, 6 = Kompressor, 7 = Kühler E-106/7, 8 = Reformer V-101 mit Wärmeübertragern E-102/3/4, 9 = Elektrischer Heizer E-105, 10 = Fackel Z-102.

Direct heated volumetric receivers: SOLASYS, SOLREF (EU FP4, FP6)

- Pressurised solar receiver,
  - Developed by DLR
  - Tested at the Weizmann Institute of Science, Israel
- Power coupled into the process gas: 220 kW_{th} and 400 kW_{th}
- Reforming temperature: between 765°C and 1000°C
- Pressure: SOLASYS 9 bar, SOLREF 15 bar
- Methane Conversion: max. 78 % (= theor. balance)
- DLR (D), WIS (IL), ETH (CH), Johnson Matthey (UK), APTL (GR), HYGEAR (NL), SHAP (I)

Qualification - Motivation

Efficiency Chain, Example: Parabolic Trough



QUARZ® – Center
Test and Qualification Center for CSP Technologies

- Strong impact on the **performance and cost efficiency**:
  - CSP component quality and durability
  - their interaction in the overall system
  - and the meteorological conditions each

- Development of **measurement techniques and devices**
- Evolution of **guidelines and standards**
  - testing methods
  - quality criteria

- Customer oriented services

  → Fundamental information for industry to
  - **Improve** quality, performance → **competiveness**
  - **Proof** of product quality → successful **market entry / bankability**

  → Consulting and training

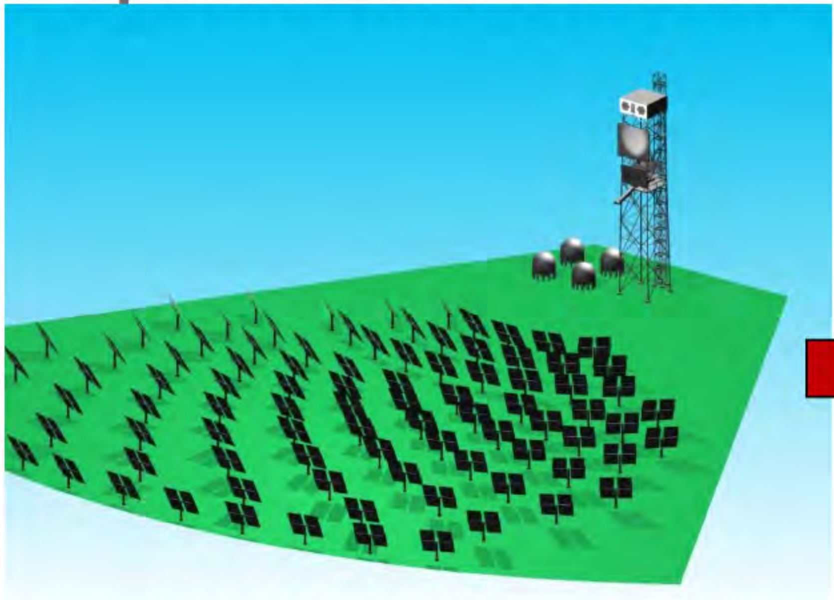
Solar Water Treatment

- 20 years of experience in solar powered Advanced Oxidation Processes (AOPs)
- Scale-up into industrial scale
- Technology is commercially available by

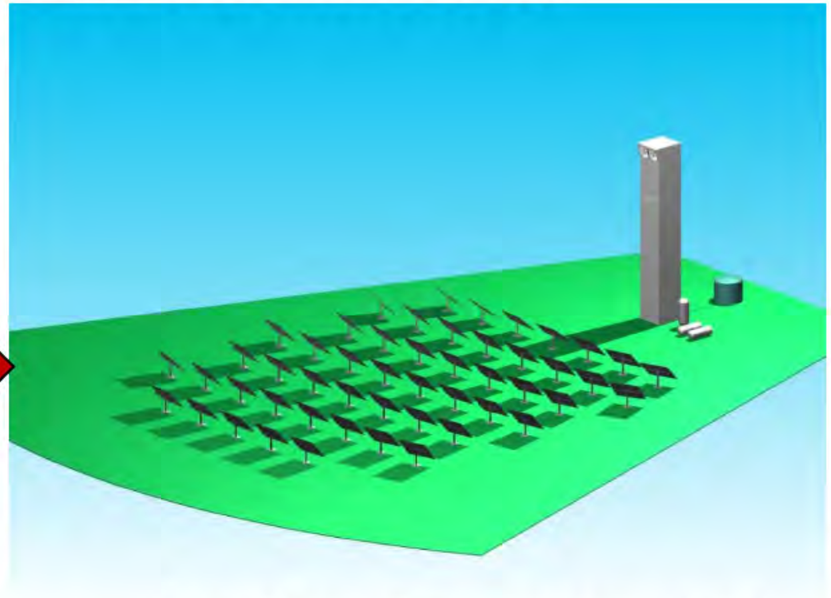
SOWΛRLΛ GmbH
Eberstadt, Germany
www.sowarla.com

DLR

Next Step:
Specific Solar Fuel Demonstration Tower needed!



CRS Tower PSA, Spain
2008 and 2015



Solar Fuels Tower, Location?
2020

- High concentration > 1000
- Heliostats fit to receiver size
- Field control adapted to fuel production processes

Thank you very much for your attention!